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SPS LABORATORIES

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July through October 1963
Contract AF33(657)-11684

"STRUCTURAL FASTENING TECHNOLOGY"

RESEARCH AND DEVELOPMENT

SPS
STANDARD PRESSED STEEL CO
JENKINTOWN, PENNSYLVANIA

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FOREWORD

This report represents the progress of the first four months through October 1963 of contract AF33(657)-11684 on "STRUCTURAL FASTENING TECHNOLOGY." The contract was issued by the Air Force Flight Dynamics Laboratory of Wright-Patterson Air Force Base, with SM/Sgt. Jesse C. Ingram of Applied Mechanics Branch, Structures Division as project engineer. The prime contract was awarded to Standard Pressed Steel Co., Jenkintown, Pennsylvania; with Vitro Laboratories of West Orange, New Jersey being a major subcontractor. The efforts of both SPS and Vitro are represented in this report.

This report was prepared by E. F. Gowen, Jr. of SPS and M. Ortner of Vitro.

ABSTRACT

A survey of available refractory materials, user refractory fastener requirements, and refractory coatings was conducted. ~~at the outset of the program.~~ The results of the survey and resultant recommendations are included in the report.

Work was started at Vitro on the actual requirements of a coated refractory fastener in a joint. TZM material with Vitro coating was used. Additional work will be forthcoming on this.

Fasteners of Cb 752 were supplied to Martin Baltimore for a structural applications study. Additional Cb 752 is on order for coating studies and a test program on electrophoretically coated threaded fasteners for mechanical properties through 2800°F.

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SECTION I

INTRODUCTION

At the present time the very hot sections of aerospace re-entry vehicles must be fabricated from refractory alloys. These must be mechanically joined because of the present unsuitability of welding and brazing to all the available refractory alloy structural materials. Other fastening means such as adhesives will not withstand re-entry temperatures.

This program was initiated to design, fabricate, coat, and test structural mechanical fastening devices having utilization capabilities up to 3600°F.

The materials for usage up to 3600°F will be refractory alloys with molybdenum, columbium, and tantalum bases.

The fasteners include threaded, deformable blind, deformable semi-blind, and other uniquely designed parts. In general, the fasteners will be multi-part and will meet the very close tolerance requirements of precision mechanical fasteners. The deformable ones will be capable of installation without degradation of the operational life.

The fasteners will be protected by electrophoretically deposited coatings. The coatings will be applicable to the substrate alloy, compatible with other existing refractory coatings, and capable of the deformation required for the function of the fastener.

Work has been progressing on mechanical structural refractory fasteners since about 1957. Many of the problems have been solved, but some remain. Examples of remaining problems to be worked on as part of this program are:

1. Actual coating requirements of a threaded fastener in a joint.
2. Applicability of coating to fastener.
3. Notch sensitivity of fasteners after coating.
4. Lack of precise dimensional control because of critical fastener tolerances.
5. Knowledge of manufacturing technique and mechanical properties of tantalum alloy fasteners.
6. Design development of deformable fasteners with high oxidation resistant integrity after deformation during installation.

The development of threaded fasteners was essentially completed in previous programs. There will be no development on molybdenum alloys or threaded fasteners of molybdenum or columbium. The multi-part deformable fasteners have historically caused difficulties because the designs of refractory parts were taken directly from steel technology with no thought to the special requirements of the refractory alloys. The deformable bolts also suffered the further handicap of having to conform to the requirements of the coating. This program will attempt to resolve these problems by either modification of existing designs or new unique designs.

There are several coatings available for refractory metals. The bulk of these are part cementation types, but other deposition methods are also available. Each coating and each coater have their own particular coating chemistry. In order to circumvent some of the difficulties involved with the multiplicity of offerings, the electrophoretic deposition technique was chosen because of its adaptability to many coating chemistries.

In general, the program is as follows:

1. Survey.

2. Requirements study.

3. Test columbium parts as a result of requirements study and adaptation of electrophoretic coating.

4. Tantalum study.

5. Deformable fastener development and evaluation.

SECTION II

SURVEY

The survey was undertaken to determine three things:

1. Requirements of ultimate fastener users as to alloy, coating, fastener configurations, usage conditions, and special requirements.

2. Coating state-of-the-art.

3. Base material availability, prices, and specifications.

The decisions made as a direct result of the survey were:

1. To use Cb 752 as one columbium based alloy.

2. To initially electrophoretically deposit the Tapco coating on the columbium bolts.

3. To investigate threaded, semi-blind, and blind fasteners through the program.

4. To undertake partial pressure studies of the coated fasteners.

5. To start a study of feasibility of coating adaptability to tantalum.

6. To use recrystallized materials throughout the program.

7. To investigate reusability characteristics of all fasteners studied.

8. To study compatability of various coatings.

A. REFRACTORY ALLOY SURVEY

The ultimate selection of refractory alloys to be used was to be based primarily on the requirements of the end item users and the desires of the Air Force based on future needs. Several materials vendors were surveyed, however, to determine such factors as new alloys, availability and price of established alloys, and working specifications. There was no attempt to run a mechanical and physical property study during the survey, as most of the intended fastener users are up to date already. The material suppliers contacted during the refractory alloy survey were:

Armetco Inc., Wooster, Ohio

Astro Metallurgical Corp., Wooster, Ohio

Climax Molybdenum Co. of Michigan

E. I. duPont de Nemours & Co. (Inc.), Wilmington, Delaware

Fansteel Metallurgical Corp., North Chicago, Illinois

General Electric Co., Cleveland, Ohio

Kawecki Chemical Co., Boyertown, Pennsylvania

Stauffer Metals Division, Richmond, California

Sylvania Electric Products Co., Towanda, Pennsylvania

Union Carbide Stellite Co., Kokomo, Indiana

Wah Chang Corp., Albany, Oregon

Westinghouse Electric Corp., Blairsville, Pennsylvania.

1. Molybdenum Based Alloys

There have been no recent advances in molybdenum based alloys which are immediately pertinent to fastener manufacture. The alloys Mo-.5 Ti and TZM (Mo-.5 Ti-.08 Zr) appear to be the best for fasteners. These are readily available with a certain amount of shelf stock, a price list, and various specifications written by both vendors and customers. The TZC alloy (Mo-1.25 Ti-.3 Zr-.15C) is still a development item.

2. Columbium Based Alloys

As a result of interest exhibited by aircraft companies, detailed information was sought on only five columbium base alloys, Cb 752 (Cb-10W-2.5 Zr), B-66 (Cb-5Mo-5V-1Zr), D 43 (Cb-10W-1Zr-.1C), FS 85 (Cb-11W-27Ta-.8Zr), and C-129-Y (Cb-10W-10Hf-.4Y). Surveys by other organizations have also included Scb 291 (Cb-10W-10Ta) and AS 55 (Cb-8W-1Zr-.7Y) in the classification of "second generation" columbium alloys. Recent noteworthy developments are the elevation of duPont's experimental alloy, X-110, to a commercial status as D43 and the improvement of Wah Chang's C-129 by the addition of yttrium. Of course, numerous older columbium base alloys are readily available, but they are of little interest as high strength fastener material.

Of the five columbium alloys of interest, only the Stellite Division of Union Carbide Corporation has a complete, detailed specification for bar and rod stock of its Cb 752 alloy. Even this is a tentative specification. Some of the alloys have specifications for sheet material only. Generally, the suppliers are willing to meet any reasonable special requirements. In order to have a common ground for comparison purposes, a brief tentative specification for columbium alloys was prepared at SPS. This specification accompanied requests for quotes on price and delivery of representative amounts of the alloys of interest.

3. Tantalum Based Alloys

Because of the relative newness of tantalum alloy development, the attempt in this program will be to delay as long as possible any final decision on a tantalum based alloy. Some information was sought from suppliers, but this will not be the last because of constant development. Alloys immediately available are Ta-10W (90-10) and T-111 (Ta-8W-2Hf). In development are Ta-8W-2Re, Ta-5W-2.5 Mo, Ta-10W-2.5Mo, Ta-17W, Ta-9.6W-2.4 Hf-.01C. It was reported (1)* that Ta-30cb-7.5V alloy has had difficulties because of vanadium segregation.

B. COATING SURVEY

During the first quarter, the following individuals and organizations were visited.

Thompson Ramo Wooldridge, Inc.	R. Jeffreys
Chance Vought Corp.	W. L. Aves, K. P. O'Kelley
McDonnell Aircraft Corp.	C. W. Neff, R. E. Jackson, J. D. Culp, D. Grimm
Boeing Co.	J. Stacey, D. Honebrink, R. Gunderson, C. Boese
Atomics International	J. P. Page, G. V. Sneesby, E. V. Kleber

*Number in parentheses refers to reference in the Bibliography

Solar	A. Stetson
Chromizing Corp.	M. Commandy.

The areas of information which were discussed included:

Current programs involving coating of refractory alloys.

Coating requirements (time, temperature, pressure, flow).

Coating chemistries and application techniques.

Coating problems peculiar to structural fasteners.

Test and inspection procedures.

Since this is not intended to be a comprehensive survey on coatings for refractory alloys, the reader is referred to several excellent existing bibliographies and reports on the subject (2 - 8) which cover the older literature.

As a result of this survey, the following conclusions were reached regarding the coatings portion of the present program:

1. The best of the state-of-the-art coating chemistries for molybdenum and columbium base alloys are unmodified molybdenum disilicide and Tapco $CbCr_2$ - $CrSi_2/TiSi_2$ system, respectively.

2. Coatings for tantalum base alloys are not as far developed as those for columbium and molybdenum. Although satisfactory reliability remains to be demonstrated, the Battelle vanadium and boron-modified silicide coating for tantalum-base alloys is superior to the tin-aluminum system. Further advancements in this area are anticipated as a result of current programs at Armour and at Solar.

3. The reported oxidation lives for the coating systems recommended in Conclusions 1 and 2 will undoubtedly be reduced when their behavior at low pressures is investigated.

4. Oxidation testing in this program should be performed at partial pressures of oxygen at least as low as 10^{-2} Torr as well as at ambient pressure.

5. Coating systems utilized for structural fasteners should be tested for compatibility with other coating systems which may be required in the total joint.

1. Coating Systems

In current usage are four main methods of coating deposition. These are slurry, pack cementation, fluidized bed, and electrophoretic. Some of these designations are listed in Table 1.

Some important characteristics of the most widely used coating application techniques are summarized in Table 2. In addition to the techniques listed, a program is currently under way at Chance Vought on modifications of the pack technique wherein the pack materials are brushed, dipped, or sprayed in layers up to 0.1 inch thick, then dried and diffused by conventional methods or by a rapid exothermic reaction. Pfaudler is currently studying fused salt deposition of chromium and titanium and modifications of existing slurry processes (4).

None of the processes listed in Table 2 is a panacea for the problems involved in coating refractory metal structures. The major advantages enjoyed by each of the techniques listed are as follows:

a. Vacuum Slurry - 1) Applicable to faying surfaces and recessed areas.

2) Coating defects relatively easily repaired.

b. Pack processes - 1) Good reliability and high temperature performance.

2) Adaptable to large structures.

c. Electrophoresis - 1) Good control of coating thickness.

2) Flexible with respect to coating composition.

d. Fluidized bed - 1) Short cycle - good control.

2) Amenable to scale-up.

While the surface preparation procedure adopted by various coating vendors differs in detail, it generally consists of the following steps:

a. Edge radiussing of sharp corners by hand grinding and polishing or by tumbling in an abrasive powder.

b. Removal of organic contaminants by solvent or detergent cleaning, followed by an acetone or water rinse.

c. Acid pickling to a maximum metal removal per surface of 0.002 inch. A typical pickling solution for columbium alloy parts which is operated at 70° - 90°F contains the following (11).

H_2SO_4 (66° Be)	- 15 vol. %
HNO_3 (42° Be)	- 10 vol. %
HF (50% Tech)	- 20 vol. %
H_2O	- 55 vol. %

Variations on this procedure which have been utilized ty Tapco (11), Pfaudler (12), and McDonnell (10) are described in the literature.

Edge radiussing is a particularly time-consuming and costly operation on large panels, and the necessity for radiussing is reflected in the widespread use of thread forms for refractory metal structural fasteners with rounded crests and roots. The use of a truncated thread form, particularly for internal threads, would be an important advance in the state-of-the-art and this possibility will be investigated in the present program.

TABLE 1

MAJOR CONSTITUENTS AND APPLICATION TECHNIQUES
OF COATINGS SYSTEMS

Coating Designation	Application Method	Elemental Constituents
General Electric LB-2	Slurry	Al, Cr, Si
General Telephone & Electronics	Slurry	Sn, Al
AMF KOTE 2	Pack Cementation	Si, B, Cr, Cb
Boeing DISIL	Fluidized Bed	Si
Chance Vought	Pack Cementation	Si, B or Si, B, Cr
Chromalloy W-2	Pack Cementation	Si, Cr
Pfaudler PFR-6	Pack Cementation	Si, Cb
Battelle	Pack Cementation	Si, B, V
TAPCO	Pack Cementation	Si, Cr, Ti
Vitro	Electrophoretic Deposition	Si, Mo, Cr

TABLE 2

CHARACTERISTICS OF SELECTED COATING APPLICATION TECHNIQUES

Coating Type	Application Method	Nominal Coating Composition	Typical Coating Cycle	Process Characteristics	Critical Parameters	Notes and References
Boeing Disil	Fluidized Powder Bed	Unmodified Silicide	TZM { 1.5 hrs @1450°F and 2 hrs @1850°F D-36 - 6 hrs @1850°F	Const. Temp process Rapid cycle No packing & unpacking of Retort	Particle Size Gas Flow Rate Fixturing for parts Temp. Uniformity	(2, 12) Fluidized Bed process in development by Pfaudler
Pfaudler PFR-6	Atmospheric Pressure Pack Cementation	Cb-modified Silicide	5 hr. heat up to 2050°F 6 hr. at 2050°F	Slow cycle Inert Filler and Activator in Pack	Particle Size a homogeneity of Pack Heat-up Time & Time at Temp. Temp. uniformity in Retort	(3, 11) W-3, Durak Band Chance-Vought Processes are similar.
TAPCO	Multicycle Vacuum Pack Cementation	$CbCr_2$ + Overlay of Cr and Ti Silicides	Cr-Ti: 8 hrs. -2200°F-1mmA	No inert Filler High Reliability	Same as PFR-6	(13)
Gen'l Electric & McDonnell LB-2(mod.)	Vacuum slurry impregnation	Al-10Cr-2Si ($CbAl_3$)	Double Coat Dry Anneal 1 hr. 1900°F	Applicable to Faying Surfaces, Recessed areas Amenable to repair Thick coating	Surface Prep'n Viscosity & Comp'n of Slurry Control of Drying and Annealing.	(9) Sn-Al Slurry Coating for Ta Developed by GTE (15)
VITRO	Electrophoretic Deposition	TZM-$MoSi_2$ Cb alloys-$CbCr_2$-$CbCr_2$/$MoSi_2$	a)Coat-2 min Rm Temp. b)Press-5-20 tsi hydrostatic c)Sinter-2 hrs 2500°F or Diffuse	a)Rapid coating cycle b)Flexible with Respect to Coating Chemistry c)High uniformity of Coating Thickness	Coating Bath Comp'n Particle Size Sintering Cond'ns	(14)

2. Coating Selection

The choice of the refractory alloy fastener and coating combination for an application is governed by many inter-related factors such as:

a Anticipated exposure conditions of the joint (time, temperature, pressure, and tensile and shear stress levels).

b. Fabricability of the alloy for the joint under consideration.

c. Compatibility requirements for alloys coated with different materials.

d. Applicability of the coating to difficult areas such as recesses, faying surfaces, and thread elements.

e. Cost which, in addition to raw materials, is determined by the fabricability of the alloy and the complexity and reliability of the coating process.

f. Applicability of a given coating system to a particular alloy composition.

These general considerations enumerated are further complicated by design problems imposed upon the fastener itself by the limitations of the available coating systems. Some of these problems are the choice of thread form (i. e. refractory, truncated, or "semi-refractory"), head design, assembly tools which will not damage the coating, logical design of blind or semi-blind mechanical fasteners which are adaptable to coating, tolerances allowed on uncoated threaded elements so that they will mate after coating, etc.

Despite this multitude of problems, a great deal of progress has been made in the utilization of coated refractory metal structural fasteners as exemplified by the recent flight of the first Asset vehicle, and the assembly and testing of structures such as McDonnell's fin-rudder assembly and simulated leading edge assemblies at Chance Vought and at other organizations. A great deal of work remains to be done, however, to develop dimensional, mechanical, and compositional standards for coated refractory alloy fasteners comparable to those which exist for uncoated fasteners, to develop coatings with sufficient ductility so that post-coating treatments after joint assembly becomes unnecessary and the use of deformable fasteners becomes practicable, and to extend the range of utilization of coated fasteners to temperatures above 3000°F at pressures below 5 Torr.

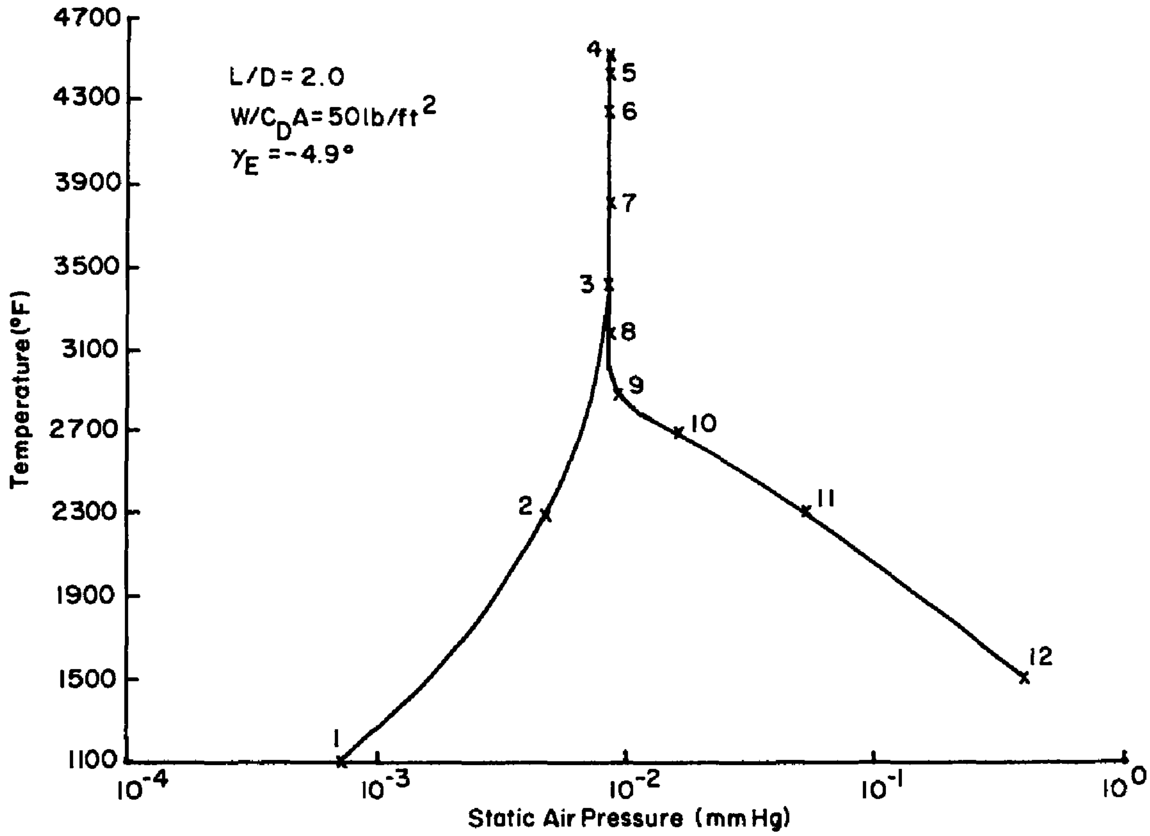
The first consideration in the choice of a refractory alloy-coating system for use in a structural fastener is the temperature-time-pressure-load-vibration requirement for the particular joint under consideration. These requirements will vary with the flight profile of the vehicle and with the position of the joint on the surface of the vehicle. Some typical anticipated equilibrium temperatures for re-entry of radiation-cooled orbital and superorbital vehicles of the glider and lifting body design are summarized in Table 3.

TABLE 3 (9)

EQUILIBRIUM TEMPERATURES FOR RADIATION COOLED RE-ENTRY VEHICLES

	Orbital (°F)		Superorbital (°F)	
	Glider	Lifting Body	Glider	Lifting Body
Nose	3600-4000	4000	6800-8300	7000-8500
Leading edge	2700-3000	-	4500-5200	-
Lower surface	1700-2400	2300-2700	2700-3750	4000-4500
Upper Surface	1500-2000	2000-2500	1800-3000	3400-4000

The dynamic conditions which exist during re-entry of a glider have been treated analytically by Perkins and others (9). Perkins' calculation of the temperature-pressure-time variations of a frontal section for one possible re-entry trajectory are shown in Figure 1. For this case peak heating from 2700° to 4500°F occurs at a pressure of 0.0085 mm Hg for a period of 25.33 min. The less severe conditions which exist at the stagnation line, and upper and lower surfaces of the leading edge during re-entry are shown in Figure 2. Here, the temperature is relatively constant for about 11 minutes of the re-entry period and peak heating occurs at a pressure of 0.1 to 1.0 mm Hg.



Point No.	Elapsed Time (min.)
1	0.66
2	1.00
3	1.33
4	1.66
5	2.50
6	5.00
7	10.00
8	20.00
9	26.66
10	33.33
11	41.66
12	50.00

FIGURE I (Reference 9)

TYPICAL REENTRY CONDITIONS AT STAGNATION POINT OF FRONTAL SECTION OF ORBITAL GLIDER

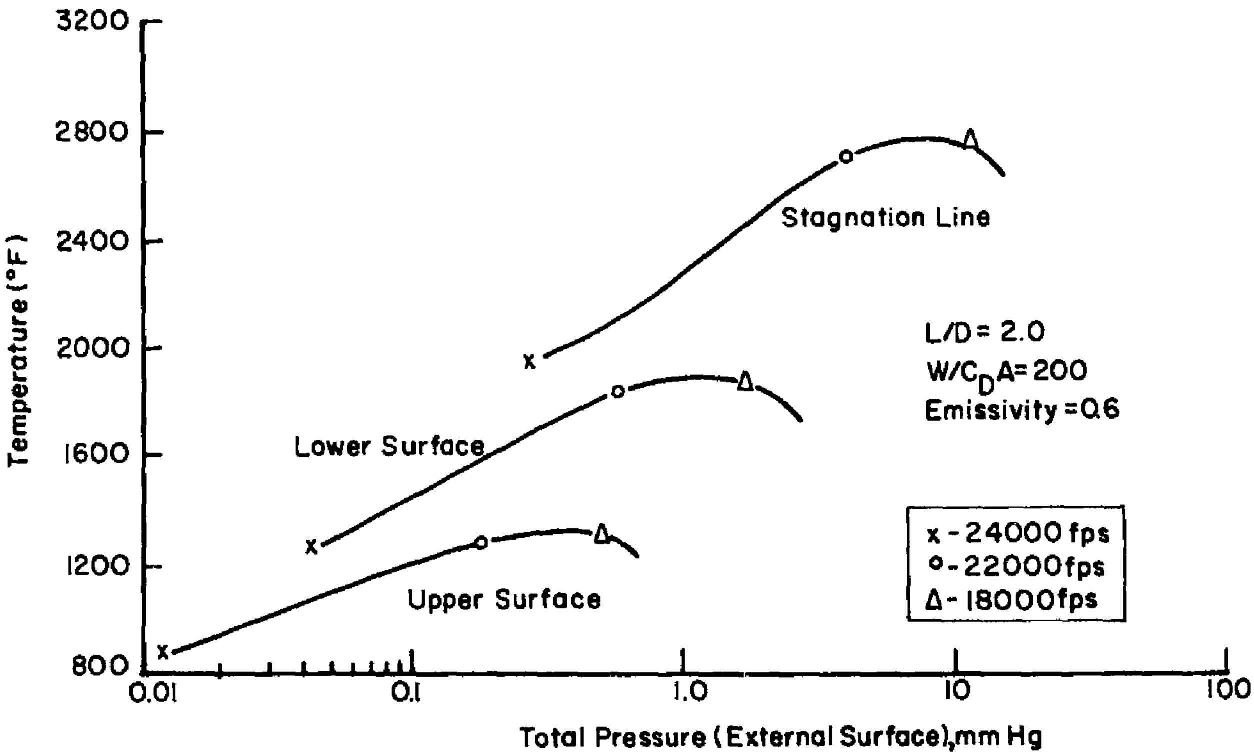


FIGURE 2 (Reference 9)

TYPICAL RE-ENTRY CONDITIONS
ALONG LEADING EDGE OF ORBITAL GLIDER

(Total elapsed time $\approx$ 20 min.)

Based upon calculations of this type and, taking into consideration the limitations of currently available coatings, materials for operational glide re-entry vehicles such as ASSET have been chosen as follows (10):

Nose cap - Zirconia

Forward leading edges - siliconized graphite

Structural members, lower forward body panels, etc. - W-3 coated TZM (Max. Svc. Temp. 3000°F)

Lower aft body panels - LB-2 coated D-14 (Max. Svc. Temp. 2500°F)

Structural Fasteners, Tubing, etc. - Tapco Coated Cb alloys (Max. Svc. Temp. 2700°F)

Molybdenum fasteners - PFR-6 or Durak B Coated TZM (Max. Svc. Temp. 3000°F)

Low temperature body panels - Uncoated L-605.

The hot external sections of Dyna Soar, on the other hand, are fabricated and fastened with Disil coated TZM, while cooler interior structural parts are fabricated from coated columbium alloys and uncoated Rene 41. This choice of materials was based upon the low pressure-high temperature performance of the available coating chemistries.

Tantalum alloys, although desirable with respect to fabricability, are not being used in current structures since the state-of-the-art in coating of tantalum-base alloys is not as far advanced as that for columbium alloys and TZM. If a reliable coating becomes available for tantalum-base alloys, then coated tantalum will probably be used for structures which are exposed at temperatures above 3000°F. This projection could change if coatings for columbium are developed with useful life under low pressure conditions at temperatures exceeding 2700°F.

3. <u>Coating Chemistry and Atmospheric Pressure Oxidation Resistance</u>

Although a large number of intermetallic compounds and most of the chemical elements have been investigated to some degree in an effort to develop oxidation resistant coatings for the refractory alloys, it is safe to say that all of the currently successful coating systems are based upon one or more of the three elements - silicon, chromium, and aluminum. The major elemental constituents contained in many of the available coatings are summarized in Table 1.

This apparent similarity in the as-applied coatings is deceptive when consideration is given to the detailed composition of the coating. The coating systems which are chemically the simplest are those in which a single coating element is used (Disil) or in which a stable intermetallic compound is applied to the metal surface (Vitro). Even in these systems, however, diffusional processes at the coating-substrate interface can result in the formation of a series of intermetallic compounds in which the concentration of coating element increases from the metal surface outward. In the molybdenum-silicon system for example the compounds Mo_3Si, Mo_5Si_3, and $MoSi_2$ may exist. The relative concentration of silicides of lower silicon content than $MoSi_2$ will increase as the coating (diffusion) time is increased. Each of these phases have been identified by NASA (18) in X-ray diffraction analysis of the AMF and Disil coatings. Multicycle pack coatings on columbium alloys are even more complex due to the increased number of coating elements and the possibility of formation of a large number of intermetallic compounds, and also the complexity of the alloy which can contribute additional elements to the coating layer through diffusion and chemical reaction. An example of a typical system of this type (Vought Si-Cr-B on Cb-1Zr) is shown in Figure 3, and the structure of the Tapco coating on a variety of columbium alloys is shown schematically in Figure 4. In the Tapco system the function of the titanium is to increase the rate of diffusion of chromium into columbium, the $CbCr_2$ acts as a barrier, preventing diffusion of columbium outward, and the complex mixture of chromium and titanium silicides provides the basic resistance to oxidation penetration through the formation of a chromia-titania-silica glassy phase.

The discussion above points up one of the possible reasons for the wide variation in the observed oxidation resistance of the available coating systems which appear superficially to be quite similar - that is the inherent oxidation resistance of the intermetallic phases which are present in the various coatings. Some of the very limited data which supports this point of view is presented in Table 4 in which the oxidation resistance of a series of related intermetallic compounds is compared. In general, those compounds of a series of intermetallic beryllides,

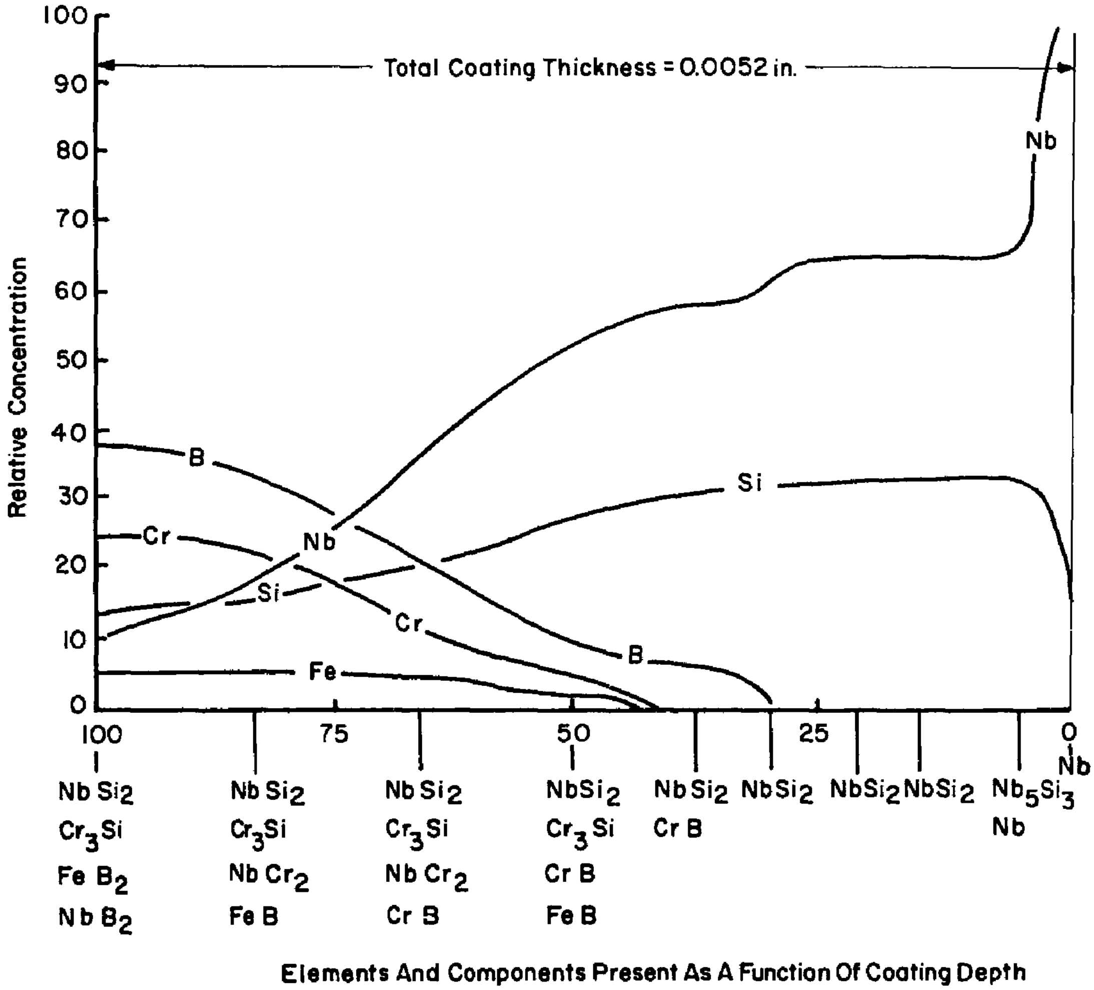


FIGURE 3

X-RAY EMISSION AND DIFFRACTION ANAYLSIS OF Si-Cr-B COATING ON Cb-1Zr (Reference 17)

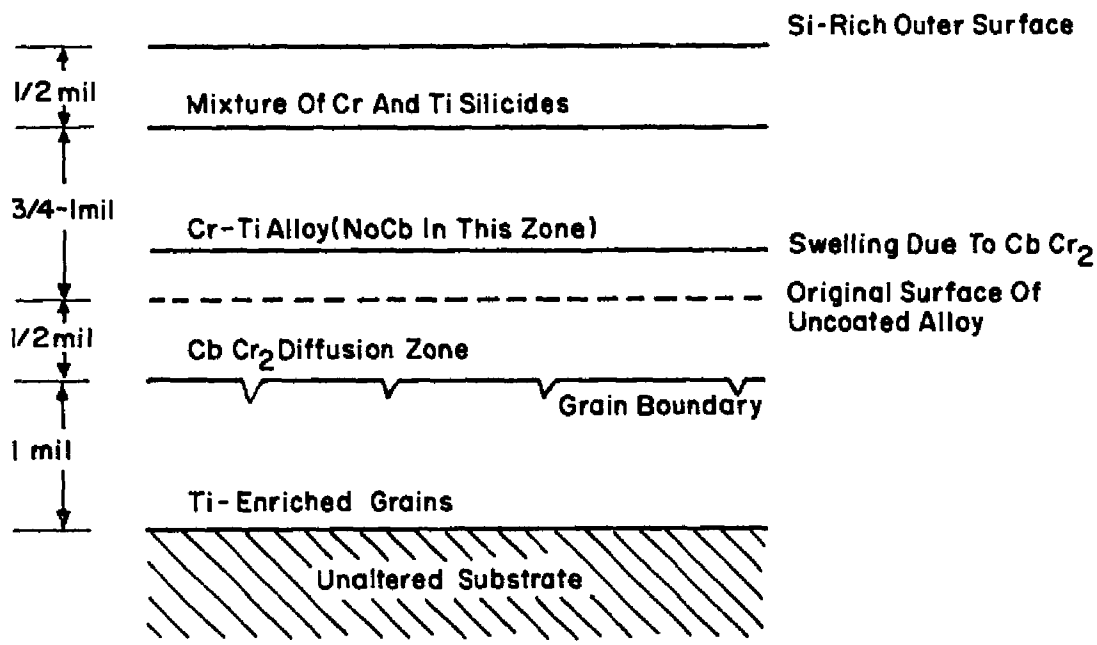


FIGURE 4

SCHEMATIC DIAGRAM OF TYPICAL Ti-Cr-Si TAPCO COATING

TABLE 4

OXIDATION RESISTANCE OF SELECTED INTERMETALLIC MOLYBDENUM, TANTALUM, AND NIOBIUM COMPOUNDS (18, 19, 20)

Compound	Density (% Theory)	Hrs	Oxidation Resistance at 2300°F in Air: Wt. Gain (mg/cm^2)	Oxidation Resistance at 2300°F in Air: Oxide Penetration (mils)
Nb_3Al	-		(negligible oxidation resistance)	
Nb_2Al	-		(negligible oxidation resistance)	
$NbAl_3$	91	25	2.4	0.3
$NbAl_3$	91	100	2.8	0.4
$TaAl_3$	91.5	25	6.4	0.8
$TaAl_3$	91.5	100	7.1	0.9
Ta_2Al, Ta_3Al	-	(No oxidation resistance at 1100°F-2400°F)		
$TaBe_{12}$	90	25	17.5	2.1
$TaBe_{12}$	90	60	18.0	2.1
Nb_5Si_3	96	1	(completely oxidized)	
$NbSi_2$	93	25	4.7	-

Phases Present	% Silicon	Wt. Change (g/cm^2) - 4-1/2 hours in air at 1500°C
$Mo + Mo_3Si$	9	-0.789
$Mo_3Si + Mo_5Si_3$	10.5	-0.693
Mo_5Si_3	16.3	-0.0516
$Mo_5Si_3 + MoSi_2$	22.6	-0.000851
$MoSi_2$	36.8	+0.00191
$MoSi_2 + Si$	40	+0.00104

silicides, or aluminides which have the highest concentration of the coating element exhibit the best oxidation resistance. Other factors, such as the effect of metal additives and substrate composition upon the viscosity and vapor pressure of the silica glass which is formed in oxidation, and unobserved coating defects undoubtedly also contribute to the variations which are observed in the performance of the coatings.

With this introduction, a compilation of data is presented in Tables 5 and 6 and Figures 5 - 7 on the atmospheric pressure cyclic oxidation resistance of several coating systems on columbium, molybdenum, and tantalum alloy sheet and foil. Intensive testing programs are continuing at NASA Langley (4) and at the University of Dayton (26), and each of the coating systems mentioned is under continuous development. In addition, new programs are under way at Solar (27) and at Armour (28) for the development of new intermetallic and/or oxide coating systems for tantalum base alloys.

4. Low Pressure Behavior of Oxidation Resistant Coatings

It was indicated previously that an external coated refractory metal structural part, during re-entry, may be exposed to low partial pressures of oxygen (0.002-0.2 mm Hg) for periods of time up to about an hour at temperatures up to 3200°F. It was first pointed out by Perkins (9) that under these conditions a silicide base coating might degrade rapidly through the loss of volatile SiO instead of protecting the substrate through the formation of solid SiO_2. Recent supporting data from Lockheed on the performance of four silicide-type coatings on molybdenum as a function of pressure are summarized in Table 7 where it is indicated that all but the Chance Vought coating suffer a decrease in maximum temperature, 30 minute oxidation life of about 450°F as the oxygen pressure is reduced from 160 Torr to 0.2 Torr.

TABLE 5

CYCLIC OXIDATION RESISTANCE OF SELECTED COATINGS ON VARIOUS COLUMBIUM ALLOY SHEET SPECIMENS (21, 22, 23)

Coating	Protective life[a] in cyclic oxidation[b], hours: 2300°F D-31	2300°F D-14	2300°F F-48	D-43	Cb	B-66	2500°F D-31	2500°F F-48	2500°F Cb	2600°F D-14	2600°F D-43	2600°F B-66
Sylcor	50	43	>300	-	28	-	20	12	24	17	-	-
	>300	150	>300	-	-	-	24	12	40	24	-	-
GE - McDonnell	176	5	24	-	12	-	24	4	2	2	-	-
	296	16	30	-	-	-	24	5	3	2	-	-
Vought	7	17	7	-	7	-	2	1	2	6	-	-
	12	18	12	-	-	-	2	2	8	13	-	-
Chromalloy	12	5	7	-	2	-	20	1	2	1	-	-
	12	16	12	-	-	-	24	1	2	9	-	-
Chromizing	7	-	24	-	24	-	6	2	2	-	-	-
	12	-	24	-	-	-	20	(c)	2	-	-	-
TRW	>300	150	>300	102	>300	>150	123	146	171	21	24	24
	>300	150	>300	148	-	-	>200	>200	>200	37	-	49
Pfaudler	-	1	-	54	-	5	-	-	-	9	5	2
	-	17	-	72	-	7	-	-	-	11	-	24

(a) First observed external rupture of the coating.
(b) 24-hr cycles to rt in the first 24 hr of test, 8 cycles to rt in every 24-hr period thereafter, at 2600°F, specimens cycled to R.T. each hr to failure.
(c) Specimen not returned.

TABLE 6

Summary of oxidation performance data for coated tantalum alloys (5)

Alloy Substrate	Coating designation	Coating thickness, mils	Oxidation life at indicated temperature (°F), hours 1200	1800	2000	2500	2700	2800	3000	3500
Ta	TRW, Cr-Ti-Si	-				>100				
	BMI, Si-Al, Si-Mn	2.9	100	20		6.5	2			
		9.7	>100	3		11	4			
Ta-10W	GTE, Al-Sn	4				100	4.2	29	>10	2
	BMI, Si-Al, Si-Mn	3.5	>100	10		3.7	10			
		7.3	40	3		>20				
Ta-10Hf-5W	GTE, Al-Sn	-			4-8	1-4				
	BMI, Si-Al, Si-Mn	2.8	100	>100		9.5	4			
		8.4	>100	1		15	7.5			
Ta-30Cb-7.5V	GTE, Al-Sn	-								
	BMI, Si	4.2	>100	>100		>20	9	8	2	

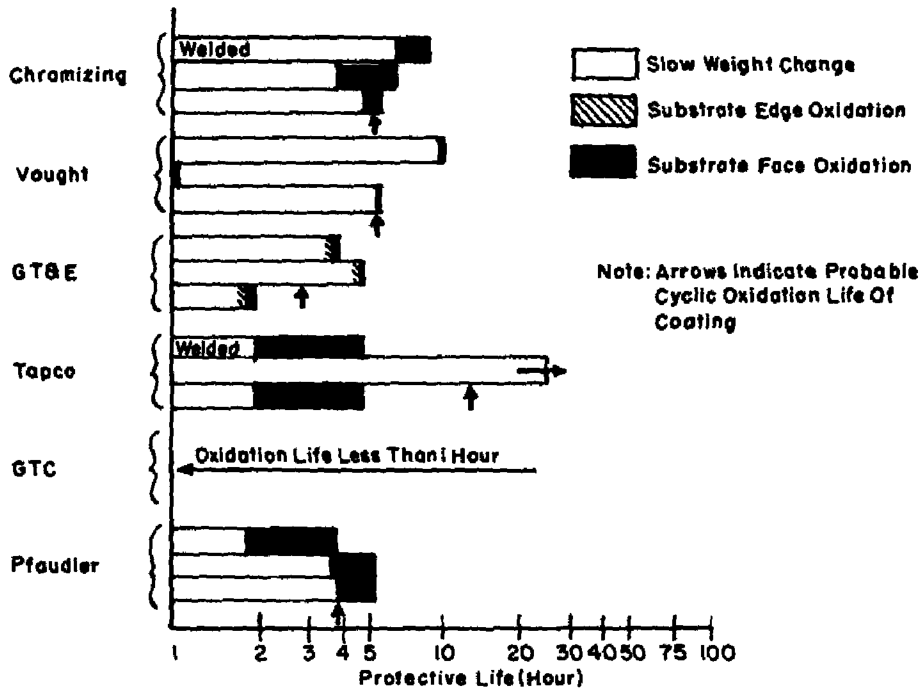


FIGURE 5

CYCLIC OXIDATION RESISTANCE OF VARIOUS COATINGS ON 6 MIL B-66 FOIL (25)

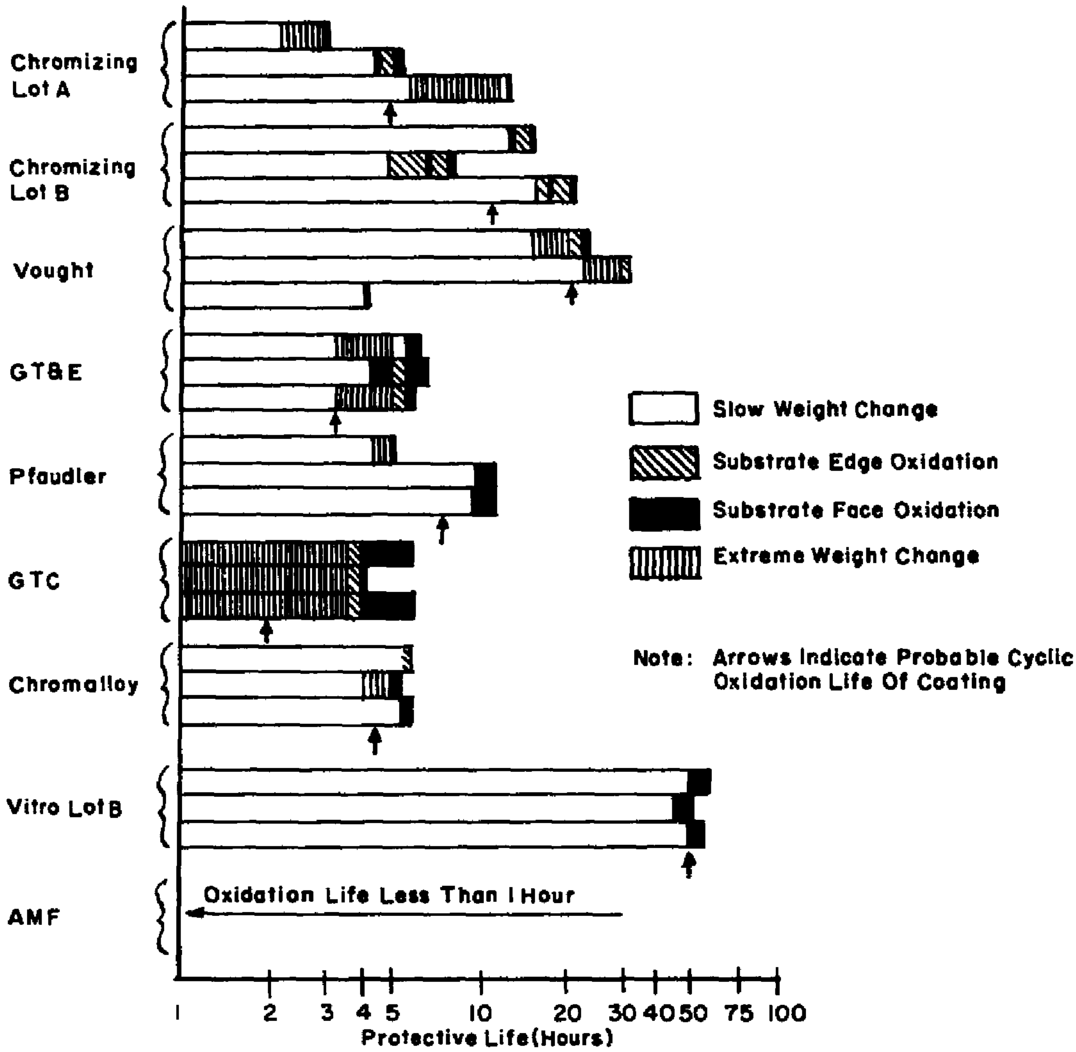


FIGURE 6

CYCLIC OXIDATION TEST AT 2500°F
OF VARIOUS COATINGS ON 6 MIL TZM FOIL (25)

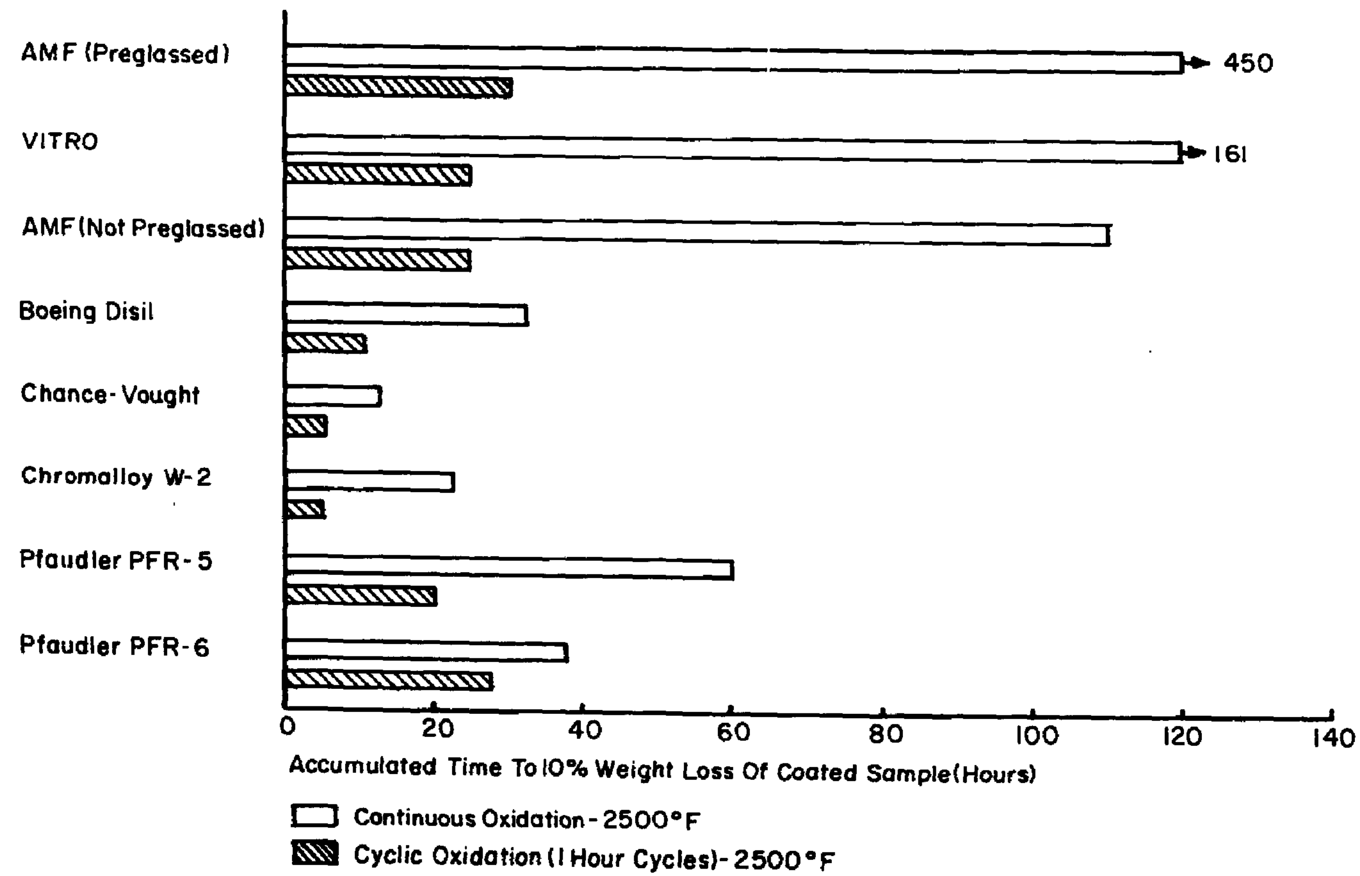


FIGURE 7

EVALUATION OF SILICIDE COATINGS ON Mo-0.5 Ti COUPONS BY A GOVERNMENT RESEARCH LAB

TABLE 7

MAXIMUM TEMPERATURE (°F) FOR 30 MINUTE LIFE
AT INDICATED OXYGEN PRESSURE (29)

Coating	Coating Thickness (mils)	Partial Pressure O_2 (mm Hg) 160	21	10	5	1	0.2
Durak B	2.8	3170	3100	-	-	2975	2815
Disil II	1.5	3280	3240	-	3225	2975	2815
PFR-6	2.6	3250	-	3200	3185	2850	2800
Chance Vought	3.0	3000	-	-	-	-	2950

The Chance Vought reduction was about 50°F, however, its maximum temperature capability for 30 minute life was some 200° - 250°F lower than the other coatings. More recently (30), Lockheed has shown that the G. T. E. tin-aluminum coating on Ta-10W will fail in less than 30 minutes at temperatures of 2540° - 3060°F when the ambient pressure is reduced to the equilibrium vapor pressure of tin (approx. 1-10 mm over the given temperature range).

Work on the low pressure behavior of the various coatings for columbium base alloys is just beginning at McDonnell, Boeing and at other organizations. Although no data has been published, preliminary results indicate that none of the available coatings is completely satisfactory for all projected requirements.

It is obvious, therefore, that the low pressure behavior of the currently available coatings is a serious problem which must be investigated in any comprehensive program involving the application of coatings to aerospace structural parts.

5. Compatibility

One of the problems in coatings, which has not been widely discussed but which is nevertheless serious, is the compatibility of the various coating systems with one another. In structures such as ASSET, special problems such as accessibility, high temperature-low pressure performance, and coating uniformity, require that two or more coating systems be used in various parts of the structure. When these coatings vary widely in their chemical makeup, each coating may be degraded by the other if they are exposed to oxidation while in contact. For example, McDonnell reported that the LB-2 and the Tapco coatings for columbium are incompatible with the PFR-6 coating for molybdenum, based upon the results of exposure of a joint containing the three systems in contact which was exposed to short time oxidation at 2000° - 2500°F. It is possible that cooler parts of a refractory structure where uncoated superalloy components are in contact with coated molybdenum or columbium parts might also evidence the same behavior.

This situation is one of several serious problems which point up the necessity for standardization in the testing and in the application of coatings for refractory structures.

C. USER SURVEY

The following companies were surveyed for comment on their future refractory fastener requirements:

Astronautics Division of General Dynamics

Boeing, Seattle

Chance Vought, Dallas

Convair, Fort Worth

Douglas, Santa Monica

Lockheed, Palo Alto

Martin, Baltimore

Marquardt, Van Nuys

McDonnell, St. Louis

North American, Downey

Republic Aviation, Farmingdale.

The major programs which are currently utilizing coated refractory metal structural fasteners in operational vehicles or in test structures are:

ASSET at McDonnell Aircraft

DYNASOAR at Boeing

SLAM at Chance Vought

Foil Gage Heat Shield Panels at Bell Aerosystems Co.

Columbium Alloy Test Panels at Martin Company, Baltimore

High Temperature Fastener Program at Republic Aviation.

Threaded fasteners for use in these programs have been fabricated from molybdenum and columbium alloys in sizes up to 3/4 inch diameter x 4 1/2 inches long, and various types of rivets have been investigated in sizes up to 5/16 inch diameter.

Because of the diversity of background, requirements, and approach to the problem, several questions were asked of each firm to get on a common ground. The questions to each of the user companies were:

1. What was the choice of

    a. molybdenum based alloy?
    b. columbium based alloy?
    c. tantalum based alloy?

2. Would these alloys be used in the recrystallized condition?

3. What coating is preferred on each of the above-mentioned alloy systems?

4. How did coating fit into the construction process?

5. Were sections recoated?

6. Were patch techniques anticipated or used?

7. What was the choice of fastener

    a. threaded?
    b. locknuts?
    c. thread form?
    d. rivets?
    e. deformable blind and semi-blind?
    f. Unique or other special fasteners?

8. What were installation considerations ?

9. What were the main design criteria for the structure ?

10. What temperature ranges were anticipated on the fasteners ?

11. Static or moving air ?

12. What atmospheric pressure considerations are made in designing the joint ?

13. What other non-refractory materials were in the joint ?

14. What are the other compatibility problems ?

15. What are current plans for fastener reusage ?

16. Are current tolerances sufficient ?

Not all companies were in position to answer all these and other questions at the time of the survey, but a good deal of information was compiled.

1. Materials

Surprisingly, most of the companies interviewed had no strong feeling on alloy selection. The choice of TZM in molybdenum based alloys was unanimous with everyone who expressed an opinion. The first choice in columbium alloys was Cb-752 which was mentioned by everyone having a choice. Two of the companies had no particular columbium alloy preference at this time. The second place columbium alloy was B-66 which was named by four of the ten as their first choice. After Cb-752 and B-66 came D-43, C-129Y, and FS-85 in that order. Only two companies were ready to mention a tantalum alloy, 90 Ta-10 W and T-111.

Most of those surveyed said that the recrystallized mechanical properties would be used in determination of design allowables. No one was firmly against this.

The accumulated comments of all parties are listed below:

Company	Molybdenum Alloy Choice	Columbium Alloy Choice	Tantalum Alloy Choice	Recrystallization
Astronautics	None	B-66, D-43, Cb 752	None	Yes
Boeing	TZM	Cb 752, C 129Y	Not ready	Yes
Chance Vought	TZM	D-43, C 129, Cb 752, B-66	Will use tungsten first	Yes
Convair	Not ready	B-66, D-43, Cb 752, FS 82	Not yet made	Yes
Douglas	TZM	B-66, FS 85, Cb 752, C 129Y	No choice	Not decided
Martin	TZM	D-43, C 129Y Cb 752	T-111	If forced
Marquardt	No choice	No choice	No choice	No choice
McDonnell	TZM	Cb 752, B-66, D-43, FS-85	90-10, T-111 Ta-30 Cb-7 1/2V	Yes
North American	No preference	No preference	No preference	Yes
Republic	Will not use	B-66, Cb 752, C 129	No preference	Yes

While the Lockheed facility at Palo Alto was included in the survey, they have no products and therefore no preferences in hardware. Their work is primarily aimed at determination of the basic mechanism of coating oxidation and breakdown under. For these reasons they were not included in the breakdown lists.

The choices above are not as pat as they appear. The Boeing selections of columbium alloys are based on availability rather than technical considerations. McDonnell lists TZM as the choice of molybdenum alloy, but their intended usage is for above 2600°F only. The McDonnel usage of materials versus temperature range is:

Molybdenum based	2600°F to 3000°F
Columbium based	to 2600°F
Tantalum based	above 3200°F
Ceramics	above 3000°F.

The McDonnell columbium alloy selections are based on strength. Martin, Baltimore takes the economy approach to refractory fastener design. Their choice of fasteners for their Test Panel Program is predicated on the cost of the raw material. For this reason Martin has considered TZM fasteners in the columbium structure. Also, C 129Y rates high with them because this alloy has been quoted at 60% of the cost of the other main second generation columbium alloys.

The Republic Aviation choice in columbium alloys was somewhat qualified since they preferred the C-129 for the high temperature ranges (2600-3000°F). Republic does not intend to use coated molybdenum based alloy fasteners in future structural work.

While Astronautics Division of General Dynamics has a preference in columbium alloys, they have no present plans to use any refractory alloy fasteners.

The selections of Chance Vought, Convair, and Douglas were based on future work. Marquardt had no choice because the bulk of their refractory structures are in uncoated tungsten alloys.

The North American engineers had no particular preference because they felt that refractory fasteners are coating critical, and that most coatings impart such great property loss that alloy selection is not of prime importance.

2. Coatings

Probably the strongest indication received from the users was that they preferred their own proprietary refractory coatings. Three of the firms contacted had coatings and others were working on their own coatings. Most felt that today's coatings were not sufficient and that future fastener coatings would be tailored more toward the exact application. Answers to direct questions were:

	Preferred Coating			
Company	Mo	Cb	Ta	Usage Comments
Astronautics	None	Tapco	None	
Boeing	Boeing	Boeing	Boeing	Have not run compatibility with other coatings

Company	Preferred Coating Mo	Cb	Ta	Usage Comments
Chance Vought	Chance Vought			Wants coated fasteners to be post-coated in structure
Convair	None	Tin-Aluminum	None	Want slurry coating
Douglas	None	Tapco	None	
Martin	None	Tapco	None	Any other coating should be compatible with Tapco
Marquardt	None	Durak B	None	
McDonnell	None	None	None	Prefer LB-2 slurry which they put on themselves. Want to see new coatings
North American	North American			NAA coating causes no loss in properties. Pest condition under 2000°F.
Republic	No preference			Want smooth coatings. Use coated fasteners, recoat structure, then patch critical areas.

All the companies with their own coating will be buying uncoated fasteners. For the most part the remaining companies desire to purchase coated fasteners. For the most part even companies which showed a preference are not completely firm on fastener coating so long as fastener coating is compatible to structure coating.

The bulk of the people contacted want coated fasteners which will be recoated after installation. Heads, nuts, and bucked portions of rivets will be patched and coated by most of the participants.

3. Fasteners

Everyone contacted had quite a bit to say about fasteners. Threaded fasteners were most popular with everyone having a certain amount of plans for them. Nine of the ten wanted rivets The deformable blind and semi-blind fasteners were more controversial. Five of the companies wanted them while two would not use them. The design philosophy varied from using deformable fasteners from minimal load (20 pounds) to the full strength of the material. Locknuts were wanted by most companies, but the inherent difficulties were recognized. Specific fastener requirements were:

Company	Threaded Designs Required	Thread Form	Size Range	Deformable Designs Required	Special Considerations
Astronautics	None	None	-	None	None
Boeing	Hex heads Flush heads Nuts (no lock) Dome nuts	Boeing spec. (equal root & crest). Flat internal crests acceptable.	#10-3/8	Rivets only. Will not use deformable or breakoff types.	To drive in flush heads.
Chance Vought	Hex & flush heads. Locknuts.	No choice	to 3/8	Rivets. Would use good ones.	Are now using own design of shear pin.
Convair	Hex & flush heads. Nuts.	No choice	No choice	No comment.	
Douglas	Hex & flush heads. Nuts.	No choice	No choice	Will use any	PLI washers considered.
Martin	Hex heads. Point drive bolts. Smooth flush heads. Nuts (locking).	Coarse preferred. No other choice.	3/16 & 1/4	Rivets. Explosive rivets.	Want locking device.
Marquardt	No choice.	No choice	No choice	Rivets & blind parts.	
McDonnell	Hex & flush heads. Dome nuts. Locknuts. Plate nuts.	Fine thread. 65% version.	#10-1/2	Any blind part. Rivet upset at room temp.	Will use jam nuts if must. Want stamped parts. Quick disconnect fastener.

Company	Threaded Designs Required	Thread Form	Size Range	Deformable Designs Required	Special Considerations
North American	Hex heads. Flush heads. Nuts.	Standard-ized coarse		Rivets blind	
Republic	Flush heads. Hex heads. Nuts.	Coarse 65% version		Rivets blind bolts.	Clips

Here, again, Astronautics, Lockheed, and Marquardt have no particular fastener requirements at this time. Marquardt does have future requirements for blind-type fasteners, but probably of a tungsten alloy.

Convair and Douglas have no present refractory structural program, but are in the concept stage of future projects. They have no firm requirements at this time.

Boeing is making use of more or less standard threaded fastener configurations in the Dynasoar effort. Their engineering evaluations have shown no need for locking devices as the coating itself acts as a lock. This is most particularly true after elevated temperature exposure. Boeing will not consider jam nuts at this time. The feeling at Boeing is quite negative on deformable type blind fasteners. They consider any effort expended as wasted.

Chance Vought has incorporated fasteners in their structural program. They had difficultirs in the bucking of molybdenum based alloy rivets. For this reason they still have reservations on rivet usage. One interesting design unique to Chance Vought is a threadless shear pin held in the joint by a cotter pin.

Martin Co., Baltimore has expressed a desire for almost every type of fastener. The first attempt at a semi-blind fastener combination is the point drive bolt with smooth countersunk head and a conventional threaded nut. The Martin desire for explosive rivets was the only one encountered in the survey. The people at Martin did express a strong desire for a locking device of some type.

The only company showing a preference for the fine thread series was McDonnell. They did express a willingness to go along with any industry standards. The people here want some type of locking device on either member. They have had previous bad experiences with coated locknuts which lost locking torque after one or two applications. McDonnell wants to use both threaded and blind fasteners to their maximum capacity. A quick disconnecting coated refractory fastener would be used at McDonnell.

North American has successfully used deformable type blind bolts in their previous refractory structural effort. They are very much interested in deformable fasteners. They are in fact replacing spot welds with coated refractory rivets. Here again the people at North American are very interested in thread standardization.

The future usage at Republic Aviation falls in line with other people's thinking. They would try to design around deformable type fasteners, but when forced to use them they would minimize the load to 20 - 50 pounds. During the course of the Air Force contract on "High Temperature Fasteners" Republic has decided on the 65% rounded refractory thread form. They do not have a long range commitment to any thread form.

4. Temperature and Atmospheric Conditions

The most popular temperatures were all under 2500°F. The discussion of temperatures at 3000°F and above was all in the future, and no firm commitment could be made at this time.

Many of the companies desire to use coated refractories at temperatures of less than 2000°F. These people would all like to see oxidation testing in the lower ranges because of the past condition prevalent with some of the coatings.

The latest studies show that coating breakdown is accelerated with lowered pressure. For this reason the consensus of opinion was that partial pressure studies must be added to the program to get meaningful data.

Some of the opinions of the survey participants were:

Company	Operating Temp. °F for Refractory Fasteners Max	Min	Atmospheric Pressures
Boeing	2700-1/2 hr		1/2 mm Hg-3000°F - 40 min.
Chance Vought	2300	1400	Partial. See Lockheed study
Convair	2300-Mo 2000-Cb		No comment
Douglas	2400-1/2 hr	1400	10^{-1}, 10^{-3}, 10^{-10}
Martin	2450-Cb, Mo 3000-Ta	2000	No comments
McDonnell	3000	1400	Room to: 3000°F-30 min-70 micron then: 1400°F-30 min-11 mm Hg
North American	2500	2000	Partial pressures
Republic	2400	1000	No comment

Here again, the people at Astronautics, Marquardt, and Lockheed had nothing direct to contribute because they do not have refractory fastener requirements. Lockheed does have a basic study (10) in which the mechanism of coating failure is being studied. This can be generally applied to fasteners, but fasteners have had no direct part in the program.

The 2700°F 1/2 hour condition mentioned by Boeing is a static air, ambient pressure test for coated fasteners. The 1/2 mm of mercury test is an evaluation of the coating whether on fasteners or other structures. This is a test to meet specific Boeing requirements. The feeling of the people at Boeing is that partial pressure studies must be added to the program to get usable data.

While Chance Vought and Douglas have had no trouble with fasteners, their interest in the Lockheed studies lead to their separate requests that partial pressure studies be added to the program.

The low pressure, high temperature cycle referred to by McDonnel is a test that will meet in flight conditions. These people feel that temperatures lower than $2000^{\circ}F$ should be thoroughly investigated.

Republic has a couple of temperature ranges of interest under $2000^{\circ}F$; these are $1500-1600^{\circ}F$ for 100 hours and $-423^{\circ}F$.

5. Applications

The information received here was both much and varied. Five companies would like to be able to retighten the nut and bolt combinations as much as one hundred (100) times without impairing oxidation resistance. In addition, most of these same people would like ten (10) to one hundred (100) missions at maximum temperature exposures. One company will not reuse fasteners.

Installation of all fasteners with existing tooling was high on the list of desirable features. Each company had their own comments peculiar to in-house procedures.

Some direct requirements were:

Company	Temp. Exposure Number	Room Reusability Number	Compatibility Coatings and Materials	General
Astronautics			Tapco coating	
Boeing	None	None	All refractory coatings. Boeing Disil especially. Super alloys	
Chance Vought	Unspecified		Vought coating	
Convair	10	Unspecified		Might use ablative fasteners
Douglas	Unspecified		Tapco	
Martin	100	100	Tapco Haynes 25 Hastalloy	
McDonnell	10	Unspecified	Lb-2	Need resistance to high torque. Water or acetone as tightening lubricant.

Company	Temp. Exposure Number	Room Reusability Number	Compatibility Coatings and Materials	General
North American	None	None	NAA coating Super alloys	
Republic	100	100	T. D. Nickel Gaseous hydrogen	Coating should prevent gas diffusion.

Most of the companies that had unspecified requirements felt that they were necessary, but that they were not ready to specify exact limits.

Boeing and North American feel that refractory alloy fasteners cannot be reused, neither after tightening at room temperature, nor after elevated temperature exposure. All the others would expect reusable fasteners out of the program.

SECTION III

MATERIAL PROCUREMENT

A. MATERIALS RECEIVED

The materials which have been obtained for the purposes of the program are listed in Table 8 along with their dimensions and chemical analyses. Bar stock was obtained for the manufacture of fasteners. Specifically, TZM parts will be used to determine coating and thread form requirements while Cb-752 parts will be used for both mechanical and oxidation testing.

B. MATERIALS SPECIFICATIONS

1. Molybdenum Alloys

In view of the fact that there are numerous specifications for TZM and since there will be limited use of it in the program, no specification for TZM was written. It was thought that Boeing Aircraft's specification for TZM was the most rigid, so material was ordered to BMS 7-99, Type IV (vacuum-cast), Class II (commercial quality surface).

2. Columbium Alloys

As mentioned previously, the alloys of interest generally do not have specifications for bar and rod stock. A tentative specification, Figure 8, and chemical composition limits, Table 9, have been prepared by SPS. The requirements of this specification are minimal, but it should be a useful starting point for negotiations with columbium alloy vendors. When this specification was distributed, there were a few comments from the vendors. One vendor suggested that the maximum allowable oxygen content should be 0.04% instead of the suggested 0.03%. Another vendor was concerned with the definition of surface contamination as opposed to surface defects. This company was reluctant to promise removal of all minor surface defects.

TABLE 8

COMPOSITION OF MATERIAL AVAILABLE FOR THE PROGRAM

Alloy	Form	Dimensions	Supplier	Heat #	Chemical Composition, % by Weight W	Zr	Ti	O	H	N	C	Mo	Cb
TZM	Bar	130"x.422"dia	Climax	7471	-	0.087	0.46	<0.0003	<0.0001	0.0012	0.018	bal	-
"	"	612"x.261"dia	"	7471	-	0.087	0.46	<0.0003	<0.0001	0.0012	0.018	"	-
Cb752	"	466"x.205"dia	Stellite	41	10.2	2.7	-	0.015	0.0006	0.004	0.007	-	bal
"	"	497"x.255"dia	"	41	10.2	2.7	-	0.015	0.0006	0.004	0.007	-	"
"	"	80.5"x.392"dia	"	41	10.2	2.7	-	0.015	0.0006	0.004	0.007	-	"
"	Sheet	18"x15"x.018"	"	8	10.49	2.54	-	0.004	0.0007	<0.010	0.003	-	"
"	"	15"x9"x.030"	"	8	10.49	2.54	-	0.004	0.0007	<0.010	0.003	-	"
D43	"	34.2"x24.8"x.012"	duPont	43-389	10.3	0.85	-	0.0178	0.0003	0.0041	0.1040	-	"
"	"	36"x24"x.030"	"	43-387*	9.4	1.0	-	0.0136	0.0003	0.0040	0.1070	-	"

* Shipping papers from duPont give Heat Number for .012 sheet as 43-387, but material itself is marked 43-389.

43-389 would seem to be correct since the two gages of D-43 sheet have different chemical analyses.

Figure 8

Tentative Specification for Columbium Alloy
Round Bar and Rod Stock

1. Scope -

1.1 This specification establishes requirements for vacuum cast, columbium base alloy round bar and rod stock. Since this is a general specification, chemical composition requirements will be specified separately.

2. Application -

2.1 This material will be used for high temperature threaded fasteners which require forging and thread rolling.

3. Technical Requirements -

3.1 Material shall be fully recrystallized with a grain size of 5 or finer as defined by ASTM E112-61.

3.2 Material shall be free of surface contamination. If necessary, processing shall include removal of sufficient material to insure removal of contaminated material as a final step.

4. Quality -

4.1 Material shall be sound, homogeneous, and free of foreign material. Material shall be free of defects such as cracks, laps, pits, and seams.

4.2 The surface of the material shall be clean and uniform. Minor surface defects may be locally removed provided such removal does not reduce the diameter below the minimum tolerance.

5. Tolerances -

5.1 The tolerance on specified diameters shall be $\pm$.005 inches.

5.2 Ordinarily random lengths will be suitable. If lengths are specified, the tolerance shall be +1/4", -0.

6. Reports -

6.1 Each shipment shall be accompanied by a shipping memorandum which reports the alloy identification, number and size of pieces, heat number, and weight.

6.2 Each shipment shall be accompanied by three copies of a test report which includes chemical composition and grain size.

7. Rejection -

7.1 Material which does not meet the requirements of this specification or negotiated modifications shall be subject to rejection.

TABLE 9

CHEMICAL COMPOSITION LIMITS* - For Columbium Base Alloys

Element	duPont D43	Fansteel FS85	Haynes Stellite Cb752	Wah Chang C-129	Westinghouse B66
Tungston	9.00 - 11.00	10.00 - 12.00	9.00 - 11.00	9.00 - 11.00	-
Tantalum	-	26.00 - 29.00	-	-	-
Zirconium	0.75 - 1.25	0.60 - 1.10	2.00 - 3.00	-	0.85 - 1.30
Vanadium	-	-	-	-	4.50 - 5.50
Molybdenum	-	-	-	-	4.50 - 5.50
Hafnium	-	-	-	9.00 - 11.00	-
Yttrium	-	-	-	0.40 Max.	-
Carbon	0.08 - 0.12	0.010 Max	0.010 Max	0.010 Max	0.010 Max.
Oxygen	0.030 Max	0.030 Max	0.030 Max	0.030 Max	0.030 Max
Nitrogen	0.015 Max	0.015 Max	0.015 Max	0.015 Max	0.015 Max
Hydrogen	0.002 Max	0.002 Max	0.002 Max	0.002 Max	0.002 Max
Columbium	Balance	Balance	Balance	Balance	Balance

* All values are percentages

C. REQUESTS FOR QUOTES ON PRICE AND DELIVERY OF COLUMBIUM ALLOYS

Numerous refractory alloy vendors were asked to quote price and delivery on two items of the columbium alloys - Cb 752, B-66, C-129, D-43, and FS-85.

Item 1 - 50 feet of .262" diameter round bar
Item 2 - 10 feet of .425" diameter round bar.

These quantities represent the approximate amount required to manufacture two hundred 1/4-20 hexagon head tension bolts with companion nuts. Such bolts would be suitable for mechanical property tests.

TABLE 10

DELIVERY TIMES OF FABRICATORS FOR COLUMBIUM BASED ROD STOCK

Alloy	Company	Delivery
Cb-752	Union Carbide	4 weeks
Cb-752	Wah Chang	7 weeks
C-129-Y	Wah Chang	6 weeks
C-129-Y	Armetco	10-12 weeks
FS-85	Fansteel	No quote
FS-85	Armetco	8-10 weeks
D-43	duPont	No quote
D-43	Armetco	10-12 weeks
B-66	Westinghouse	4 weeks

SECTION IV

FASTENERS

The fasteners initially were required for the requirements study, the Martin, Baltimore program, and the electrophoretic coating adaptability study on columbium. All these were threaded bolts and nuts. Any final decision on deformable fasteners will be made later in the program.

A. REQUIREMENTS STUDY

The fasteners in the requirements study were threaded 1/4-20 hexagon heads and their companion nuts. These are shown in Figures 9 through 12. The thread form was either the rounded root and crest as shown in Figure 13 or a truncated version thereof.

B. MARTIN, BALTIMORE

Martin, Baltimore fastener requirements were conceived separate from this program. Martin needed hexagon heads (Figure 14), flush heads (Figure 15), and companion shear nuts (Figure 16). The flush heads were Point Drive Bolts which required the broaching of a hexagon socket in the point of the bolt. This operation had never been accomplished before. Hexagon sockets had been forged into the head of countersunk bolts.

These parts were coated one-half with Tapco coating and one-half with Vitro coating.

C. COATING ADAPTABILITY STUDY

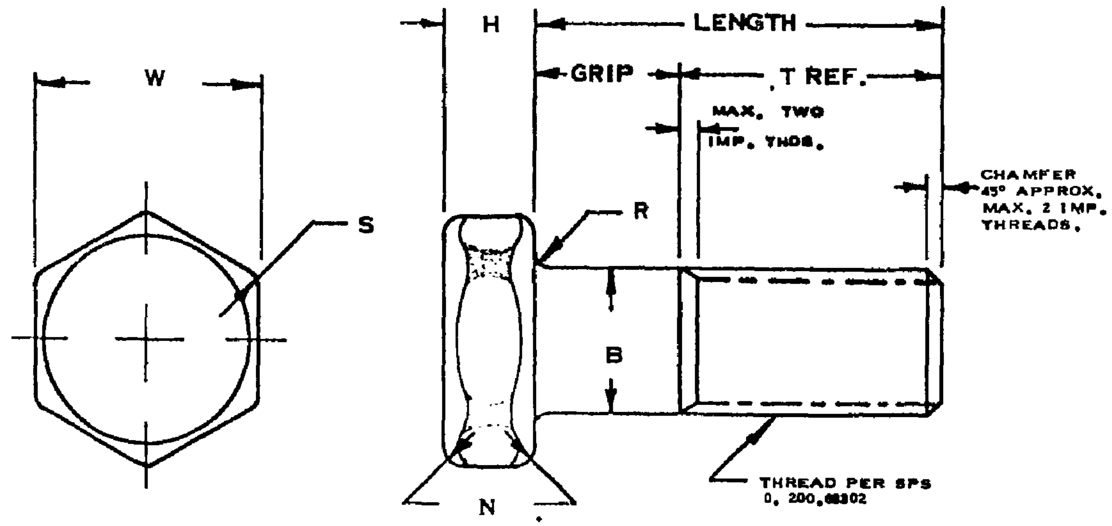
A fastener configuration will be chosen from the results of the requirements study.

SPS STANDARD PRESSED STEEL COMPANY
PRECISION FASTENER DIVISION

SHEET 1 OF 1

DRAWING NUMBER SD.300.63305

REVISION



THREAD	B	H	N RAD.	R RAD.	S RAD.	T REF.	W	X	Y
1/4–20	.2444 .2439	.167 .137	.035 .020	.018 .020	.040 .025	.500	[illegible] .428	.008	.0045

NOTES:

1. MATERIAL: MOLYBDENUM ALLOY
2. FINISH: [illegible] COATING .0016–.0024 THICK.
3. CONCENTRICITY: HEAD AND BODY WITHIN "X" T.I.R.
   BODY AND THREAD P.D. WITHIN "Y" T.I.R.
4. PART NUMBERS: THE BASIC PART NUMBER IS 63305.
   FIRST DASH NUMBER DESIGNATES DIAMETER IN SIXTEENTHS.
   SECOND DASH NUMBER DESIGNATES GRIP LENGTH IN SIXTEENTHS.
   EXAMPLE:
   63305–4–8 = 1/4–20 BOLT, .500 GRIP, 1.000 LONG.
5. GRIP LENGTHS AVAILABLE IN 1/16TH. INCH INCREMENTS, LENGTH = NOMINAL GRIP + T.
6. DIMENSIONS BEFORE COATING.
7. SURFACE ROUGHNESS PRIOR TO COATING; BODY, BEARING SURFACE OF HEAD, THREAD ROOT, AND SIDES OF THREADS, 32 MICRO INCHES – OTHER SURFACES, 125 M.I. PER MIL–STD–10 .

TOLERANCES: AND UNLESS OTHERWISE NOTED

STANDARDS AND SPECIFICATIONS	TITLE	DRAWN BY L. L. S. DATE 10/30/63
	BOLT, HEXAGON HEAD, REFRACTORY MATERIAL	APPROVED RTS DATE 10/30/63
CUSTODIAN: JENKINTOWN, PA.		PART NUMBER 63305

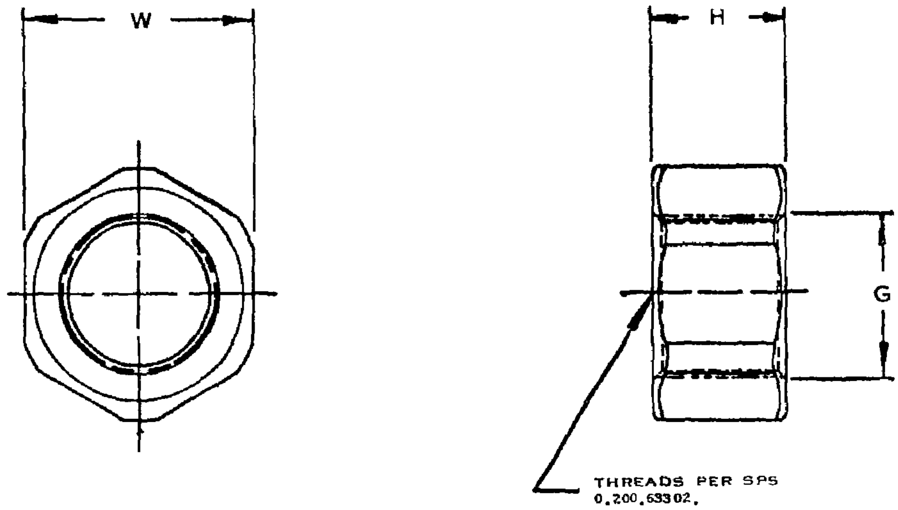
FIGURE 9

STANDARD PRESSED STEEL COMPANY
PRECISION FASTENER DIVISION

SHEET 1 OF 1

DRAWING NUMBER SD. 300. 63322

REVISION



		H	G	W	
PART NO.	THREAD	±.009	+.024 −.000	MAX.	MIN.
63322	1/4−20	.255	.252	.371	.364

NOTES:

1. MATERIAL: MOLYBDENUM ALLOY.
2. FINISH: VITRO COATING .0016−.0024
3. DIMENSIONS APPLY BEFORE COATING.
4. ROUND ALL SHARP EDGES.

TOLERANCES ± AND UNLESS OTHERWISE NOTED

STANDARDS AND SPECIFICATIONS	TITLE	DRAWN BY L. L. S. DATE 11/1/63
	NUT, HEXAGON, HEAVY HIGH TEMPERATURE	APPROVED RTS DATE 11/1/63
CUSTODIAN: JENKINTOWN, PA.		PART NUMBER 63322

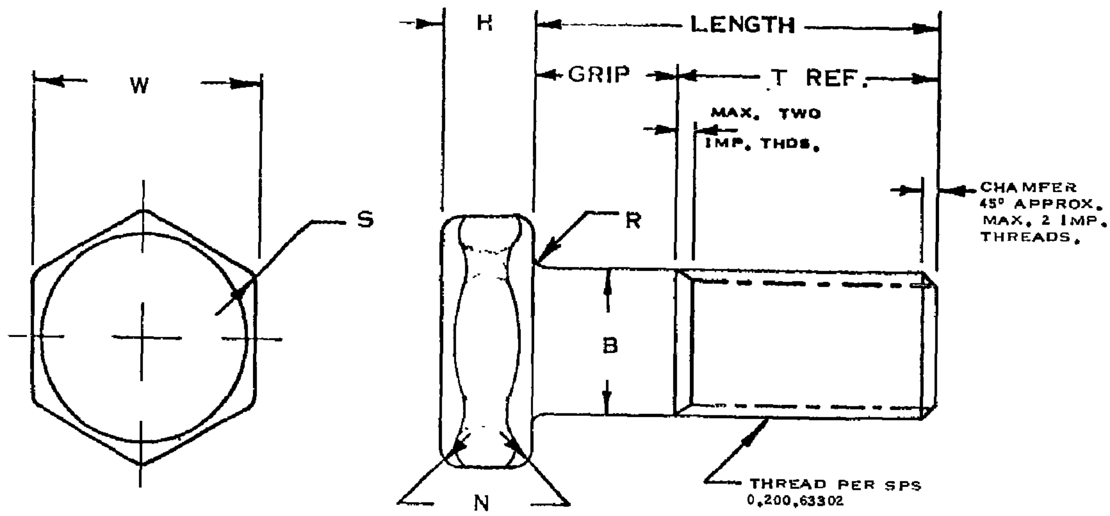
FIGURE 10

SPS STANDARD PRESSED STEEL COMPANY
PRECISION FASTENER DIVISION

SHEET 1 OF 1

DRAWING NUMBER SD.300.63306

REVISION



THREAD	B	H	N RAD.	R RAD.	S RAD.	T REF.	W	X	Y
1/4-20	.2444 .2439	.167 .137	.035 .020	.020 .010	.040 .025	.503	.435 .425	.008	.0045

NOTES:

1. MATERIAL: COLUMBIUM ALLOY.
2. FINISH: VITRO COATING. .0016 - .0024 THICK.
3. CONCENTRICITY:
   HEAD AND BODY WITHIN "X" T.I.R.
   BODY AND THREAD P.D. WITHIN "Y" T.I.R.
4. PART NUMBERS:
   THE BASIC PART NUMBER IS 63306
   FIRST DASH NUMBER DESIGNATES DIAMETER IN SIXTEENTHS.
   SECOND DASH NUMBER DESIGNATES GRIP LENGTH IN SIXTEENTHS.
   EXAMPLE:
   63306-4-8 = 1/4-20 BOLT, .500 GRIP, 1.003 LONG.
5. GRIP LENGTHS AVAILABLE IN 1/16TH. INCH INCREMENTS, LENGTH = NOMINAL GRIP + T.
6. DIMENSIONS ARE BEFORE COATING.
7. SURFACE ROUGHNESS PRIOR TO COATING: BODY, BEARING SURFACE OF HEAD, THREAD ROOT, AND SIDES OF THREADS, 32 MICRO INCHES - OTHER SURFACES, 125 M.I. PER MIL-STD-10

TOLERANCES: AND UNLESS OTHERWISE NOTED

STANDARDS AND SPECIFICATIONS	TITLE	
	BOLT, HEXAGON HEAD, REFRACTORY MATERIAL	DRAWN BY L. L. S. DATE 10/30/63 APPROVED RTS. DATE 10/30/63 PART NUMBER 63306
CUSTODIAN JENKINTOWN, PA.		

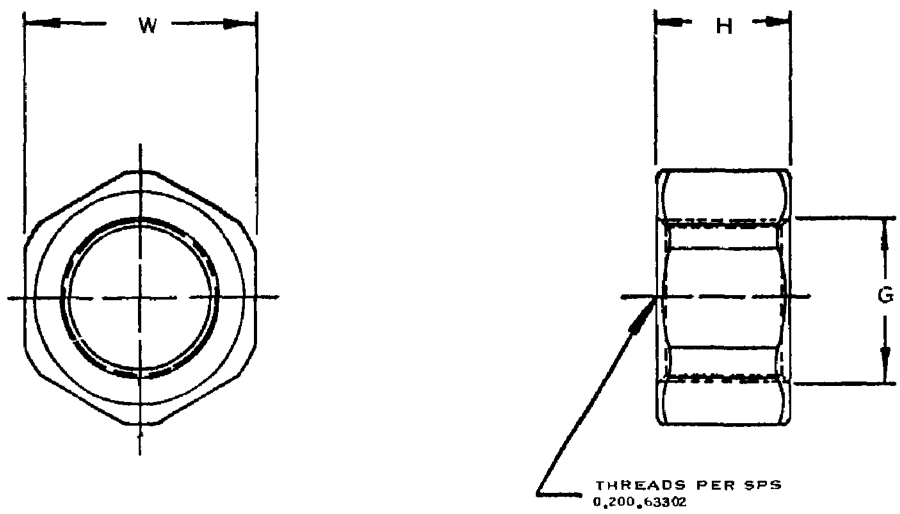
FIGURE 11

STANDARD PRESSED STEEL COMPANY
PRECISION FASTENER DIVISION

SHEET 1 OF 1

DRAWING NUMBER SD.300.63321

REVISION



		H	G	W	
PART NO.	THREAD	−.009	+.0[illegible] −.000	MAX.	MIN.
63321	1/4−20	.255	.252	.371	.364

NOTES:

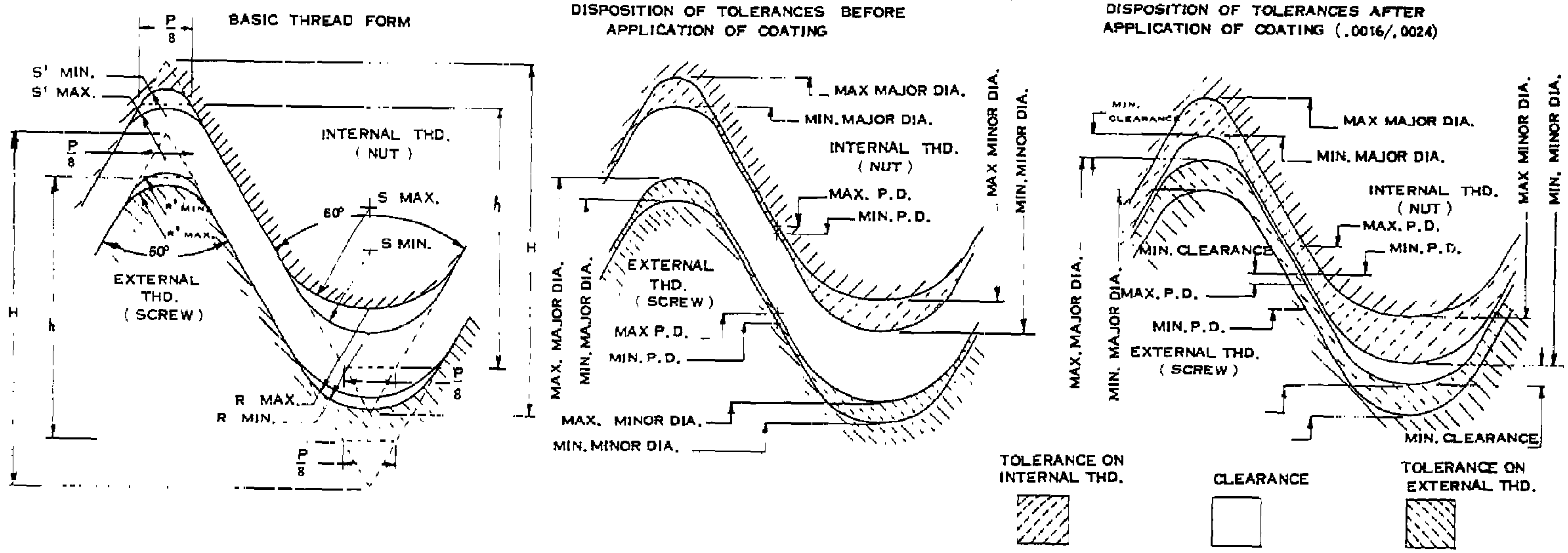
1. MATERIAL: COLUMBIUM ALLOY
2. FINISH: VITRO COATING .0016−.0024 THICK.
3. DIMENSIONS APPLY BEFORE COATING.
4. ROUND ALL SHARP EDGES.

TOLERANCES: AND UNLESS OTHERWISE NOTED

STANDARDS AND SPECIFICATIONS	TITLE	DRAWN BY L. L. S. DATE 11/1/63
	NUT, HEXAGON, HEAVY HIGH TEMPERATURE	APPROVED RTS DATE 11/1/63
CUSTODIAN JENKINTOWN, PA.		PART NUMBER 63321

FIGURE 12

0 ● 200 ● 63302 | REVISION AND DATE



SIZE	EXTERNAL THREAD								INTERNAL THREAD								MINIMUM CLEARANCES AFTER COATING		
	BEFORE COATING					AFTER COATING			BEFORE COATING					AFTER COATING					
	R	R'	MAJOR DIA.	PITCH DIA.	MINOR DIA.	MAJOR DIA.	PITCH DIA.	MINOR DIA.	S	S'	MAJOR DIA.	PITCH DIA.	MINOR DIA.	MAJOR DIA.	PITCH DIA.	MINOR DIA.	MAJOR DIA.	PITCH DIA.	MINOR DIA.
#10-24	.0093	.0054	.1827	.1547	.1373	.1875	.1619	.1421	.0108	.0049	.2028	.1722	.1578	.1996	.1674	.1546	.0040	.0010	.0040
	.0081	.0041	.1786	.1532	.1332	.1818	.1580	.1364	.0084	.0028	.1963	.1701	.1509	.1915	.1629	.1461			
1/4-20	.0112	.0064	.2428	.2093	.1884	.2476	.2165	.1932	.0130	.0059	.2636	.2269	.2096	.2604	.2221	.2064	.0037	.0010	.0037
	.0097	.0049	.2380	.2076	.1836	.2412	.2124	.1868	.0101	.0033	.2561	.2247	.2017	.2513	.2175	.1969			
5/16-18	.0124	.0072	.3055	.2682	.2450	.3103	.2754	.2498	.0145	.0066	.3270	.2862	.2670	.3238	.2814	.2638	.0034	.0010	.0034
	.0107	.0054	.3002	.2664	.2398	.3034	.2712	.2430	.0113	.0037	.3185	.2836	.2580	.3137	.2764	.2532			
3/8-16	.0140	.0081	.3681	.3262	.3000	.3729	.3334	.3048	.0163	.0074	.3902	.3444	.3228	.3870	.396	.3196	.0032	.0010	.0032
	.0121	.0061	.3622	.3242	.2942	.3654	.3290	.2974	.0127	.0041	.3809	.3416	.3128	.3761	.3344	.3080			

SCREW THREADS, 65$ WITH MANDATORY ROOT AND CREST RADIUS, FOR REFRACTORY ALLOY MATERIALS AND .002 VITRO COATING.

TOLERANCE UNLESS SPECIFIED
FRACTIONS ±
DECIMALS ±
ANGLES ±
SURFACE FINISH

SPS
STANDARD PRESSED STEEL COMPANY
JENKINTOWN, PENNSYLVANIA ● SANTA ANA, CALIFORNIA

DRAWN BY R. SHEAFFER
10/30/63

MATERIAL AND HEAT TREAT

FIGURE 13

STANDARD PRESSED STEEL COMPANY
PRECISION FASTENER DIVISION

SHEET 1 OF 1

DRAWING NUMBER SD.300.63308

REVISION

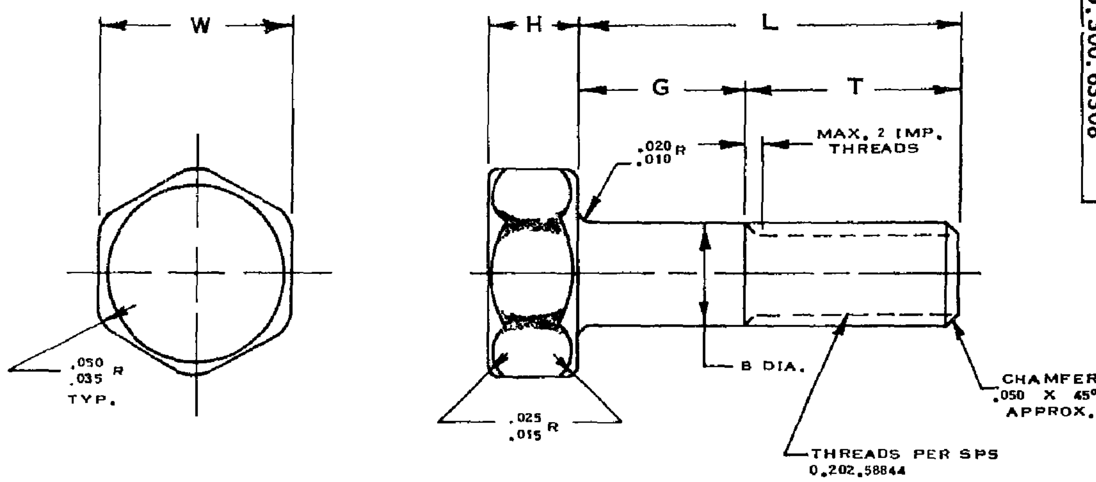


TABLE I

PART NO.	THREAD	B DIA.	G ±.010	H	L ±.015	T REF.	W
63308-3-005	10-24 NS	.189 .186	.156	.141 .109	.498	.342	.377 .365
63308-3-007	10-24 NS	.189 .186	.220	.141 .109	.562	.342	.377 .365

NOTES:

1. MATERIAL: CB752 COLUMBIUM ALLOY.
2. FINISH: VITRO OR TAPCOCOATING .0021-.0029 THICK.
3. SURFACE ROUGHNESS PRIOR TO COATING:
   ROOT AND SIDES OF THREADS AND BODY 32 M.I.,
   OTHER SURFACES 125 M.I.
4. CONCENTRICITY: THREAD P.D. AND BODY DIAMETER WITHIN .0045 T.I.R.
5. ROUND ALL SHARP EDGES .010 MINIMUM.
6. PART NUMBERS:
   63308 IS THE BASIC PART NUMBER.
   FIRST DASH NUMBERM DESIGNATES DIAMETER AND THREAD PER TABLE I.
   SECOND DASH NUMBER DESIGNATES NOMINAL GRIP LENGTH TO NEAREST 1/32ND.
   EXAMPLE:
   63308-3-005 = 10-24 NS BOLT, .156 GRIP, .498 LONG.
   63308-3-007 = 10-24 NS BOLT, .220 GRIP, .562 LONG.

TOLERANCES: .010 AND 2° UNLESS OTHERWISE NOTED

STANDARDS AND SPECIFICATIONS	TITLE	DRAWN BY L.L.S. DATE 11/4/63
	BOLT, HEXAGON HEAD HIGH TEMPERATURE	APPROVED R.T.S. DATE 11/4/63
CUSTODIAN: JENKINTOWN, PA.		PART NUMBER 63308

329

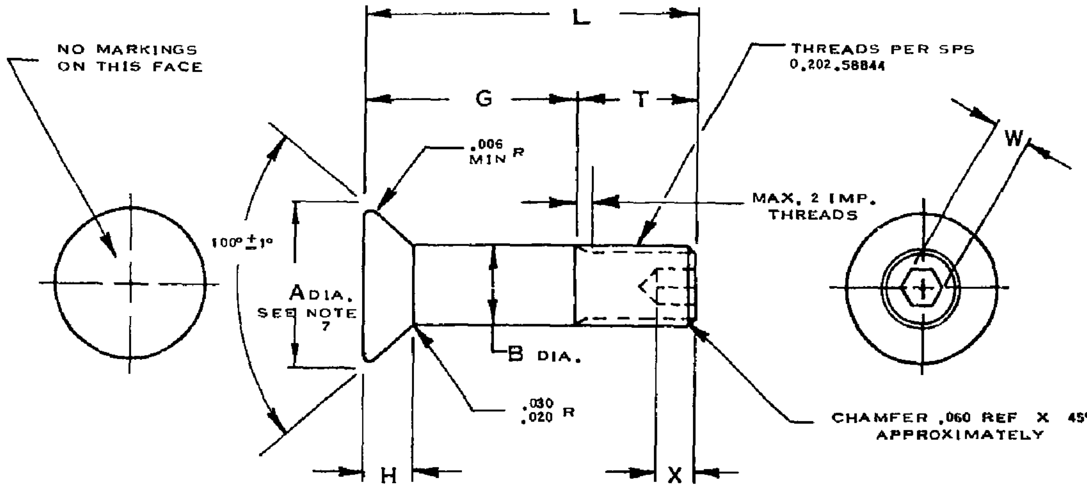
FIGURE 14

SPS STANDARD PRESSED STEEL COMPANY
PRECISION FASTENER DIVISION

SHEET 1 OF 1

DRAWING NUMBER SD.300.63301

REVISION



PART NO.	THREAD	A DIA.	B DIA.	G ±.010	H REF.	L +.031 −.016	T REF.	W	X MIN.
63301-4-009	1/4-20 NS	.402 .322	.2490 .2460	.262	.063	.709	.447	.095 .094	.156

NOTES:

1. MATERIAL: CB752 COLUMBIUM ALLOY
2. FINISH: VITRO OR TAPCO COATING, .0021-.0029 THICK
3. SURFACE ROUGHNESS PRIOR TO COATING: FLAT AND CONICAL SURFACES OF HEAD, ROOT, AND SIDES OF THREADS AND BODY, 32 M.I., OTHER SURFACES 125 M.I.
4. CONCENTRICITY: CONICAL SURFACE OF HEAD AND BODY DIAMETER WITHIN .002 T.I.R. THREAD P.D. WITH BODY DIAMETER WITHIN .0045 T.I.R.
5. ROUND ALL SHARP EDGES .010 R MINIMUM.
6. PART NUMBER CONSISTS OF BASIC PART NUMBER WHICH IS 63301 AND TWO DASH NUMBERS. FIRST DASH NUMBER DESIGNATES DIAMETER IN SIXTEENTHS. SECOND DASH NUMBER DESIGNATES GRIP LENGTH, IN 1/32NDS CLOSEST TO NOMINAL GRIP. EXAMPLE:

   63301-4-009 = 1/4-20 NS BOLT, .262 GRIP, .709 LONG.

7. A MAX EQUALS THEORETICAL MAX SHARP CORNER, MIN IS ABSOLTUE MINIMUM WITH RADIUS.

TOLERANCES ± .010 AND 2° UNLESS OTHERWISE NOTED

STANDARDS AND SPECIFICATIONS	TITLE	
	BOLT, SPECIAL FLUSH HEAD	DRAWN BY L.L.S. DATE 11/4/63
		APPROVED R.T.S. DATE 11/4/63
CUSTODIAN JENKINTOWN, PA.		PART NUMBER 63301

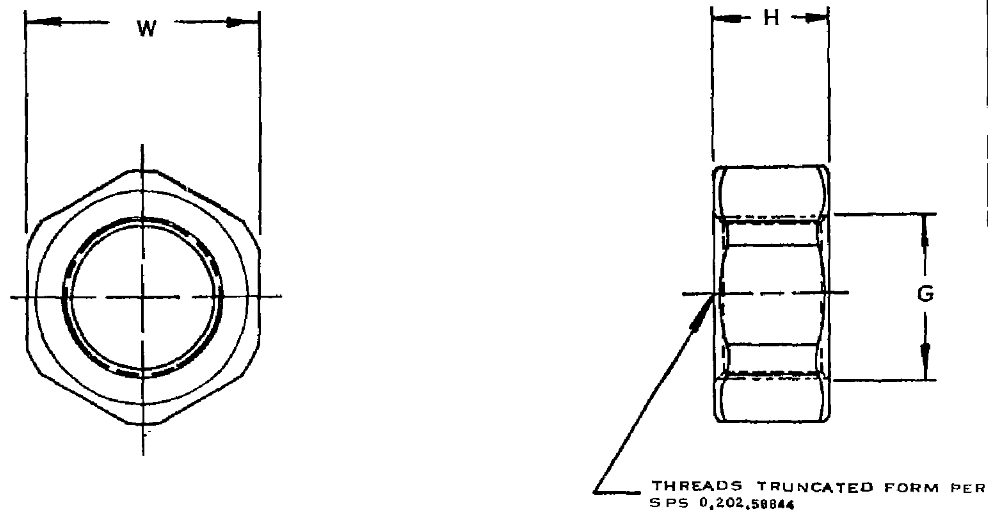
FIGURE 15

sps STANDARD PRESSED STEEL COMPANY
PRECISION FASTENER DIVISION

SHEET 1 OF 1

DRAWING NUMBER SD,300,63303

REVISION



PART NO.	THREAD	H ±.009	G +.024 −.000	W MAX.	W MIN.
63303−1024	.190−24 NS	.173	.192	.370	.360
63303−420	.250−20 NS	.204	.252	.433	.426

NOTES:

1. MATERIAL: COLUMBIUM ALLOY − CB752
2. FINISH: VITRO OR TAPCO COATING .0021 − .0029 THICK.
3. DIMENSIONS APPLY BEFORE COATING.
4. ROUND ALL SHARP EDGES, EXCEPT THREAD CREST.

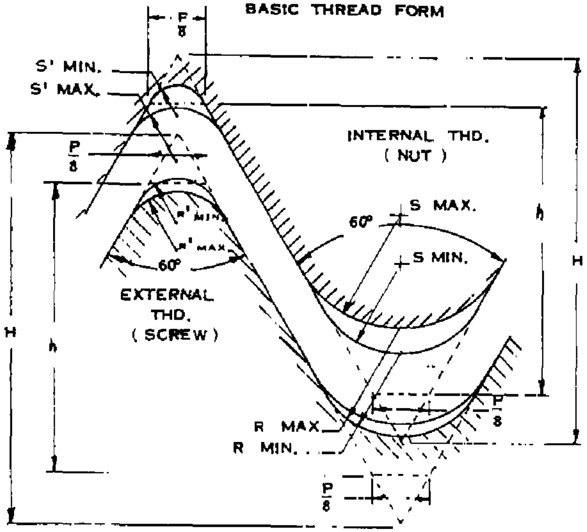
TOLERANCES: AND UNLESS OTHERWISE NOTED

STANDARDS AND SPECIFICATIONS	TITLE	DRAWN BY L.L.S. DATE 11/4/63
	NUT, HEXAGON, THIN HIGH TEMPERATURE	APPROVED R.T.S. DATE 11/4/63
CUSTODIAN: JENKINTOWN, PA.		PART NUMBER 63303

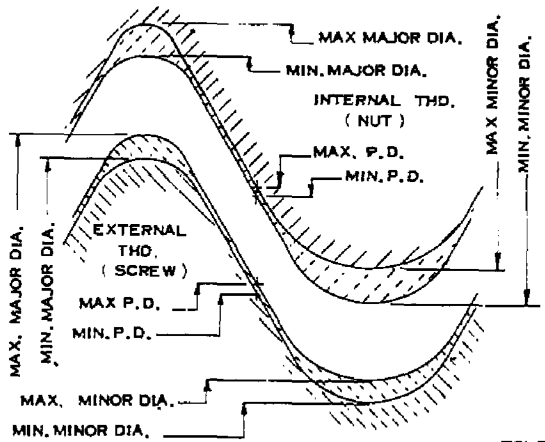
FIGURE 16

0 ● 202 ● 58844 | REVISION AND DATE

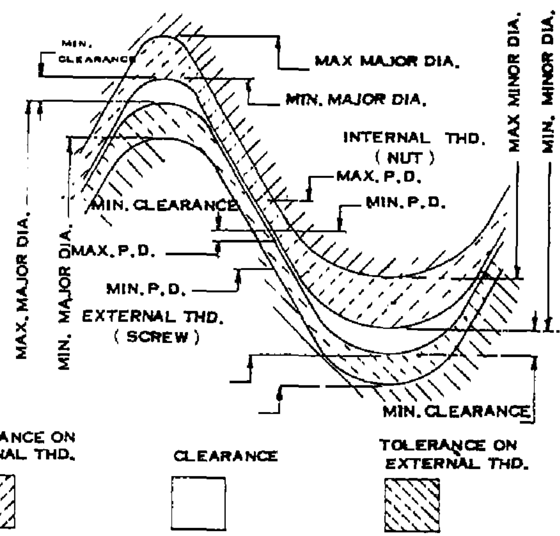
BASIC THREAD FORM



DISPOSITION OF TOLERANCES BEFORE APPLICATION OF COATING



DISPOSITION OF TOLERANCES AFTER APPLICATION OF COATING (.0021/.0029)



SIZE	EXTERNAL THREAD — BEFORE COATING: R	R'	MAJOR DIA.	PITCH DIA.	MINOR DIA.	AFTER COATING: MAJOR DIA.	PITCH DIA.	MINOR DIA.
#10-24	.0093	.0054	.1812	.1532	.1358	.1870	.1619	.1416
	.0081	.0041	.1771	.1517	.1317	.1813	.1580	.1359
1/4-20	.0112	.0064	.2413	.2078	.1869	.2471	.2165	.1927
	.0097	.0049	.2365	.2061	.1821	.2407	.2124	.1863
5/16-18	.0124	.0072	.3040	.2667	.2435	.3098	.2754	.2493
	.0107	.0054	.2987	.2649	.2383	.3029	.2712	.2425
3/8-16	.0140	.0081	.3666	.3247	.2985	.3724	.3334	.3043
	.0121	.0061	.3607	.3227	.2927	.3649	.3290	.2969

SIZE	INTERNAL THREAD — BEFORE COATING: S	S'	MAJOR DIA.	PITCH DIA.	MINOR DIA.	AFTER COATING: MAJOR DIA.	PITCH DIA.	MINOR DIA.	MINIMUM CLEARANCES AFTER COATING: MAJOR DIA.	PITCH DIA.	MINOR DIA.
#10-24	.0108	.0049	.2043	.1737	.1593	.2001	.1674	.1551	.0050	.0010	.0050
	.0084	.0028	.1978	.1716	.1524	.1920	.1629	.1466			
1/4-20	.0130	.0059	.2651	.2284	.2111	.2609	.2221	.2069	.0047	.0010	.0047
	.0101	.0033	.2576	.7262	.2032	.2518	.2175	.1974			
5/16-18	.0145	.0066	.3285	.2877	.2685	.3243	.2814	.2643	.0044	.0010	.0044
	.0113	.0037	.3200	.2851	.2595	.3142	.2764	.2537			
3/8-16	.0163	.0074	.3918	.3459	.3243	.3876	.3396	.3201	.0042	.0010	.0042
	.0127	.0041	.3824	.3431	.3143	.3766	.3344	.3085			

SCREW THREADS, 65% WITH MANDATORY ROOT AND CREST RADIUS FOR REFRACTORY ALLOY MATERIALS
TAPCO COATING

TOLERANCE UNLESS SPECIFIED
FRACTIONS ±
DECIMALS ±
ANGLES ±
SURFACE FINISH

SPS — STANDARD PRESSED STEEL COMPANY
JENKINTOWN, PENNSYLVANIA ● SANTA ANA, CALIFORNIA

MATERIAL AND HEAT TREAT

DRAWN BY J. MINNICK
DATE 4-4-62

FIGURE 17

SECTION V

COATINGS

A. ELECTROPHORETIC COATING OF COLUMBIUM BASE ALLOYS

On the basis of the survey, the Tapco Cr-Ti-Si coating was chosen for application to columbium-base alloy structural fasteners by means of the electrophoretic technique. This coating, which is applied by Tapco in a two-step vacuum pack cementation process, consists of a diffusion barrier (approximately 0.5 mil thick) of $CbCr_2$ plus a second layer which contains a complex mixture of the silicides of chromium and titanium. The major phases present in the silicide layer and their relative concentrations are not known with certainty but are believed to be $CrSi_2$ and $TiSi_2$. Based upon a recommendation by Tapco, the electrophoretic adaption of the outer layer of the Cr-Ti-Si coating will be investigated over the following range of concentrations: 100% $CrSi_2$, 90 $CrSi_2$-10$TiSi_2$, 75 $CrSi_2$-25 $TiSi_2$, and 50 $CrSi_2$-50 $TiSi_2$. Spectrographic analyses of the chromium, $CrSi_2$, and $TiSi_2$ powders used in this study are shown in Table 11.

The $CbCr_2$ diffusion barrier was formed by two electophoretic methods:

1. Approximately 3 mils of a mixture of 95% chromium and 5% alumina were codeposited on the columbium alloy substrate. The coating was then diffusion annealed for one to three hours in argon at 1375°C and the excess chromium was peeled from the substrate.

2. Approximately three mils of pure chromium were deposited on the columbium alloy substrate and heat treated as above. After heating, the coating was dipped in a solution of 1:1 hydrochloric acid to dissolve the excess chromium.

Photomicrographs of the $CbCr_2$ diffusion barrier formed by these techniques on D-36 and on Cb-752 are shown in Figures 18, 19, and 20.

The static oxidation life of a 0.5 mil layer of $CbCr_2$ on Cb-752 sheet was checked at 2600°F out of curiosity. The sample failed in two hours.

Work is now underway to establish sintering conditions for the deposition of the various mixtures of $CrSi_2$-$TiSi_2$ over the $CbCr_2$ diffusion barrier.

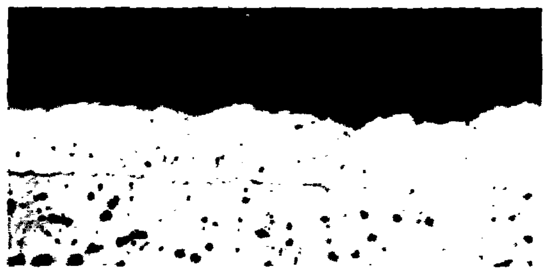
TABLE 11

SPECTROGRAPHIC ANALYSIS OF $CrSi_2$ and $TiSi_2$ POWDER (wt % max.)

	$TiSi_2$	$CrSi_2$	Cr
SILVER	ND<0.001%	ND<0.001%	
ALUMINUM	0.03%	0.2%	0.1
ARSENIC	ND<0.05%	ND<0.05%	
GOLD	ND<0.05%	ND<0.05%	
BORON	0.007%	0.007%	
BARIUM	ND<0.001%	ND<0.001%	
BERYLLIUM	ND<0.001%	ND<0.001%	
BISMUTH	ND<0.001%	ND<0.001%	0.005
CALCIUM	ND<0.005%	ND<0.005%	
CADMIUM	ND<0.05%	ND<0.05%	
COBALT	0.005%	ND<0.001%	
CHROMIUM	0.007%	High	High
COPPER	0.05%	0.005%	0.01
IRON	0.1%	0.3%	0.2
GALLIUM	ND<0.001%	ND<0.001%	
GERMANIUM	ND<0.005%	ND<0.005%	
HAFNIUM	ND<0.05%	ND<0.05%	
INDIUM	ND<0.001%	ND<0.001%	
IRIDIUM	ND<0.05%	ND<0.05%	
LITHIUM	ND<0.05%	ND<0.05%	
MAGNESIUM	0.005%	0.007%	
MANGANESE	0.01%	0.02%	
MOLYBDENUM	0.07%	0.02%	0.03
SODIUM	ND<0.05%	ND<0.05%	
COLUMBIUM	0.007%	0.01%	
NICKEL	0.003%	0.007%	
OSMIUM	ND<0.05%	ND<0.05%	
LEAD	ND<0.003%	ND<0.003%	
PALLADIUM	ND<0.001%	ND<0.001%	0.01
PLATINUM	ND<0.005%	ND<0.005%	
RHODIUM	ND<0.005%	ND<0.005%	
RUTHENIUM	ND<0.05%	ND<0.05%	
ANTIMONY	ND<0.05%	ND<0.05%	
SILICON	High	High	0.1
TIN	ND<0.001%	ND<0.001%	0.001
STRONTIUM	ND<0.001%	ND<0.001%	
TANTALUM	0.05%	ND<0.05%	
TELLURIUM	ND<0.1%	ND<0.1%	
THALLIUM	ND<0.01%	ND<0.01%	
TITANIUM	High	0.007%	
VANADIUM	0.003%	0.01%	
TUNGSTEN	ND<0.05%	ND<0.05%	
ZINC	ND<0.03%	ND<0.03%	
ZIRCONIUM	0.02%	0.03%	

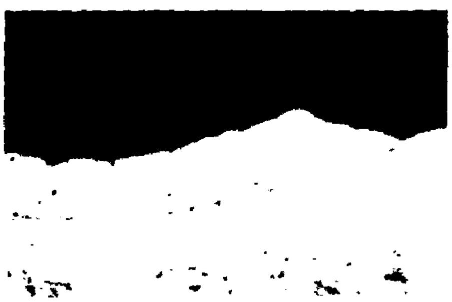
600X

Figure 18 Cr-Al_2O_3 Process on Cb-752
2.5 hours @ 1375°C



600X

Figure 19 Cr-Al_2O_3 Process on D-36 3 hours @ 1375°C



600X

Figure 20 Cr Process on D-36
2 hours @ 1375°C

B. ELECTROPHORETIC COATING UNIFORMITY AND CORRELATION OF MEASUREMENTS AT SPS AND VITRO

In order to check the uniformity of the electrophoretic coating for molybdenum alloys, and to compare the results of pitch diameter and body diameter measurements made at both Vitro and SPS, a group of seven 1/4-20 TZM studs were fabricated at SPS. The studs were approximately two inches long with a one-half inch length of thread at each end. Each stud was stamped at one end with an identifying letter which also served as an index mark. The pitch diameter of each sample was then measured at four indexed points on the second and sixth threads at each end, and body diameter measurements were made at two points on the shank. The pitch diameter was measured at SPS with a Pratt and Whitney No. 35 TRI Roll Thread Comparator equipped with Type 5 rolls, and the body diameter was determined with a Brown and Sharpe No. 245 Indicating Bench Micrometer. The studs were then sent to Vitro where the measurements were repeated with a duplicate set of instruments after calibrating Vitro's TRI Roll Gage against a master setting plug whose pitch was accurately determined at the SPS Metrology Laboratory. The studs were then coated under identical conditions at Vitro to a nominal thickness of 2.5 mils, and the pitch diameter and body diameter measurements were repeated at both Vitro and SPS.

All of the measurements are listed in Tables 12 and 13. It will be noted from the data of Table 12 that uncoated sample numbers A, B, C, and R, Q, S, and K represent two groups whose pitch diameters differ by 0.003 - 0.004 inch. The body diameters of all seven samples shown in Table 13, however, represent a single statistical population. The arithmetic means ($\bar{x}$), variances (s^2), standard deviations (s), and number of measurements (n) from which these statistics were derived are summarized in Table 14.

To test the hypothesis that the means of the measurements made at SPS and at Vitro are equal, the "t-test" is used (31). Although the equality of the measurements is almost self-evident from the data of Table 14, a sample calculation will be made for the measurements of the pitch diameter of samples R, Q, S, and K, after coating, taken at SPS ($\bar{x}_1$) and at Vitro ($\bar{x}_2$).

$$t = (\bar{x}_1 - \bar{x}_2) \quad / Sp \quad (n_1 + n_2 / n_1 n_2)^{1/2}, \text{ where}$$

$$Sp^2 = s_1^2 \,(n_1 - 1) + S_2^2 \,(n_2 - 1)/n_1 + n_2 - 2$$

TABLE 12

ELECTROPHORETIC COATING OF 1/4-20 TZM STUDS
COMPARISON OF PITCH DIAMETER MEASUREMENTS AT SPS AND VITRO

		Letter End P.D. x 10^4 in.				Plain End P.D. x 10^4 in.			
		Letter Up		Lowest Reading		Letter Up		Lowest Reading	
Sample	Measurement*	2nd Th'd	6th Th'd	2nd Th'd	6th Th'd	2nd Th'd	6th Th'd	2nd Th'd	6th Th'd
	SB	2082	2083	2082	2083	2081	2082	2081	2082
A	VB	2078	2084	2075	2083	2077	2086	2075	2081
	VC	2139	2139	2136	2136	2139	2142	2133	2137
	SC	2146	2141	2145	2138	2142	2143	2140	2140
	ΔPD(SPS)	0064	0058	0063	0055	0061	0061	0059	0058
	SB	2081	2080	2080	2080	2080	2082	2080	2081
B	VB	2079	2082	2075	2079	2080	2080	2079	2079
	VC	2142	2139	2136	2135	2136	2134	2131	2131
	SC	2139	2136	2136	2133	2132	2137	2130	2135
	ΔPD(SPS)	0058	0056	0056	0053	0052	0055	0050	0054
	SB	2077	2076	2076	2075	2077	2077	2076	2077
C	VB	2068	2076	2066	2074	2076	2077	2074	2076
	VC	2134	2135	2130	2132	2136	2134	2135	2132
	SC	2137	2131	2136	2130	2137	2133	2135	2131
	ΔPD(SPS)	0060	0055	0060	0055	0060	0056	0059	0054
	SB	2118	2118	2115	2113	2119	2118	2116	2115
R	VB	2121	2118	2112	2113	2119	2118	2118	2116
	VC	2180	2176	2174	2171	2175	2168	2173	2167
	SC	2178	2174	2172	2169	2175	2168	2172	2165
	ΔPD(SPS)	0060	0056	0057	0056	0056	0050	0056	0050
	SB	2118	2118	2115	2115	2119	2115	2113	2111
Q	VB	2120	2117	2116	2115	2117	2118	2105	2111
	VC	2178	2175	2173	2169	2170	2169	2167	2167
	SC	2180	2174	2174	2170	2176	2170	2171	2165
	ΔPD(SPS)	0062	0056	0059	0055	0057	0055	0058	0054
	SB	2117	2113	2115	2112	2120	2118	2114	2112
S	VB	2115	2113	2110	2112	2116	2114	2114	2112
	VC	2176	2173	2171	2170	2178	2173	2173	2168
	SC	2172	2173	2169	2168	2178	2177	2171	2167
	ΔPD(SPS)	0055	0060	0054	0056	0058	0059	0057	0055
	SB	2111	2111	2108	2110	2111	2113	2108	2109
K	VB	2113	2112	2109	2110	2114	2112	2109	2109
	VC	2179	2170	2176	2169	2175	2174	2170	2170
	SC	2174	2165	2173	2164	2170	2169	2167	2166
	ΔPD(SPS)	0063	0054	0065	0054	0059	0056	0059	0057

*LEGEND S = SPS C = After Coating
V = Vitro B = Before Coating

TABLE 13

ELECTROPHORETIC COATING OF 1/4-20 TZM STUDS

COMPARISON OF BODY DIAMETER MEASUREMENTS AT SPS AND VITRO

Sample	Measurement*	Letter End O.D. x 10^5 in.	Plain End O.D. x 10^5 in.	Coating Thickness** = $\frac{\Delta O.D.}{2}$ x 10^5 in. Letter End	Plain End
	SB	24673	24732		
A	VB	24651	24750		
	VC	25115	25205	232	228
	SC	25115	25197		
	SB	24723	24652		
B	VB	24731	24640		
	VC	25253	25090	261	225
	SC	25241	25160		
	SB	24650	24723		
C	VB	24651	24731		
	VC	25203	25324	276	297
	SC	25168	25290		
	SB	24729	24714		
R	VB	24740	24718		
	VC	25200	25190	230	236
	SC	25209	25188		
	SB	24714	24728		
Q	VB	24729	24743		
	VC	25208	25179	240	218
	SC	25223	25215		
	SB	24719	24735		
S	VB	24722	24743		
	VC	25254	25255	266	256
	SC	25243	25263		
	SB	24717	24725		
K	VB	24718	24721		
	VC	25221	25239	252	259
	SC	25245	25223		

LEGEND: S = SPS B = Before Coating
*V = Vitro C = After Coating

**Based upon Vitro measurement

TABLE 14

Analysis of Dimensional Measurements AT SPS and Vitro on 1/4-20 TZM Studs

	$\bar{x}$	$s^2 \times 10^8$	$s \times 10^4$	n
SPS Measurements Before Coating (in.)				
P.D. (Samples A, B, C)	0.2080	6.57	2.5625	24
P.D. (Samples R, Q, S, K)	0.2114	11.68	3.417	32
O.D.	0.24709	8.34	2.89	14
SPS Measurements After Coating (in.)				
P.D. (Samples A, B, C)	0.2137	21.00	4.582	24
P.D. (Samples R, Q, S, K)	0.2171	17.74	4.212	32
ΔP.D.	0.0057	10.91	3.303	56
O.D.	0.25213	20.92	4.574	14
Vitro Measurements Before Coating (in.)				
P.D. (Samples A, B, C)	0.2077	20.74	4.554	24
P.D. (Samples R, Q, S, K)	0.2114	13.74	3.707	32
O.D.	0.24713	13.85	3.720	14
Vitro Measurements After Coating (in.)				
P.D. (Samples A, B, C)	0.2136	10.91	3.303	24
P.D. (Samples R, Q, S, K)	0.2172	13.84	3.720	32
O.D.	0.25210	34.41	5.866	14
Coating Thickness $= \frac{\Delta O.D.}{2}$	0.00248	4.99	2.234	14

For the special case $n_1 = n_2$, the formulae reduce to:

$$t = (\bar{x}_1 - \bar{x}_2)/Sp\ (^2/n_1)^{1/2} \text{ and } Sp^2 = 1/2\ (s_1^2 + s_2^2)$$

From Table 10:

$$S_p^2 = 1/2\ (17.74 + 13.84)\ 10^{-8} = 15.79 \times 10^{-8}$$

$$S_p = 3.97 \times 10^{-4}$$

$$t = 1 \times 10^{-4}/3.97 \times 10^{-4}\ (1/4) = 1.01$$

Since the calculated value of t does not exceed the critical value of $t_c = 2.66$, the hypothesis that the means of the measurements made at the two laboratories are equal may be accepted at the 99% confidence level. Finally, since there is no difference between the measurements made at each laboratory, all values obtained for the increase in pitch diameter and for the coating thickness may be considered a single statistical population. The 99% confidence ($M_{99\%}$) intervals about the mean of these values can then be derived from Table 13 as follows:

$$M_{99\%} = \bar{x}_i \pm 2.58\ s_i/n_i^{1/2}, \text{ or}$$

Δ Pitch Diameter=0.0057±2.58(3.3x10^{-4})/7.48=0.0057±0.00011 in.

Coating Thickness=0.00248±2.58(2.2x10^{-4})3.74=0.00248± 0.00015 in.

The tolerance intervals shown below for a determination, at either laboratory, of the coating thickness or of the increase in pitch diameter due to the coating will include 95% of the measurements at a confidence level of 0.95.

Tolerance limits for Δ pitch diameter=0.0057±(2.35) (3.303) 10^{-4}= 0.0057±0.00077.

Tolerance limits for coating thickness=0.00248±(3.012) (2.234) 10^{-4} = 0.00248± 0.00067.

The significance of these calculations is that thread measurements made at either SPS or at Vitro may be accepted with confidence by the other facility. Furthermore, the variances in body diameter and in pitch diameter of the as-fabricated fastener do not significantly increase in magnitude as a result of application of the molybdenum disilicide coating. In all cases, the uniformity of the coating is within the limits of accuracy of the instruments employed and the variability which is inherent in the rolled thread.

SECTION VI

THREAD FORM REQUIREMENTS STUDY

One of the first objectives of the experimental program will be to determine the thread form which will be employed for the refractory metal fasteners which will be manufactured under this contract. Since there was some evidence, based upon previous work, that an electrophoretically deposited coating could be reliably applied to a conventional truncated thread, an experiment was set up to compare the oxidation life of external and internal coated threads of refractory (radiussed crests and roots) and truncated design, both in the unassembled condition and in a simple joint.

The following TZM parts will be furnished to Vitro by SPS for electrophoretic coating with unmodified molybdenum disilicide:

Part Description	Thread Form	Number of Parts
1/4-20 TZM nut	refractory	9
1/4-20 TZM nut	truncated	9
1/4-20 TZM hex head bolt	refractory	9
1/4-20 TZM hex head bolt	truncated	9
TZM collar	not applicable	12

After coating to a dimensional build-up of 0.0020 $\pm$ 0.0004 inch, the samples will be oxidation tested by Vitro in triplicate, at 2600^{o}F in slowly moving air at one atmosphere pressure in the following conditions:

	No. Parts (incl. collar)
Unassembled nuts and bolts of each thread form	12
Joint - refractory thread form nut and bolt	9
Joint - truncated thread form nut and bolt	9
Joint - truncated nut and refractory bolt	9
Joint - truncated bolt and refractory nut	9

The coated joints will be torqued to 25 in.-lbs. before oxidation testing. Three extra parts of each type of nut and bolt will be coated and sent to

SPS for comparative tests at 2600°F in slowly moving air and in air flowing at a linear velocity of 250 f. p. s. On the basis of these tests a thread form will be chosen for additional tests of coated TZM joints with coating thicknesses ranging from one to three mils.

In preparation for this experiment, a few pounds of molybdenum disilicide powder were purchased and analyzed as shown in Table 15. Since a check of the material indicated that the particle size was too coarse to yield a satisfactory electrophoretic dispersion, the powder was ball-milled under isopropanol for 48 hours in a chrome manganese steel mill, then dried and leached twice with dilute sulfuric acid to reduce the iron content indicated in Table 15. The acid treatment reduced the iron content to 0.2%. The ratio by weight of molybdenum to silicon was also determined and found to be 1.77 as compared to the theoretical value of 1.71. The ball-milled powder yielded a satisfactory dispersion. Coating and testing of the samples should be completed by December.

TABLE 15

SPECTROGRAPHIC ANALYSIS OF MOLYBDENUM DISILICIDE
(ND = not detected)

SILVER	ND<0.001%
ALUMINUM	0.04%
ARSENIC	ND<0.05%
GOLD	ND<0.05%
BORON	0.01%
BARIUM	ND<0.001%
BERYLLIUM	ND<0.001%
BISMUTH	ND<0.001%
CALCIUM	ND<0.005%
CADMIUM	ND<0.05%
COBALT	0.05%
CHROMIUM	0.5%
COPPER	0.05%
IRON	MEDIUM - (1.76% by wet analysis)
GALLIUM	ND<0.001%
GERMANIUM	ND<0.005%
HAFNIUM	ND<0.05%
INDIUM	ND<0.001%
IRIDIUM	ND<0.05%
LITHIUM	ND<0.05%
MAGNESIUM	0.01%
MANGANESE	0.03%
MOLYBDENUM	HIGH
SODIUM	ND<0.05%

SECTION VII

DEFORMATION STUDIES

The work on deformation is aimed at the eventual choice or design of blind and semi-blind deformable fasteners. At this time the molybdenum alloys are not being included in the program. Because of availability, work has started on deformation of sheet of D-43 and Cb-752.

The results of bending uncoated sheet are shown in Fig. 21, 22, 23, and 24.

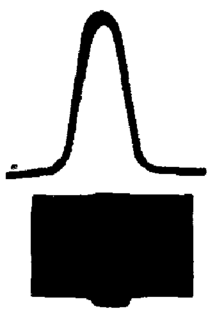


FIGURE 21
Deformed Specimen
D-43 Material
.030 Gage

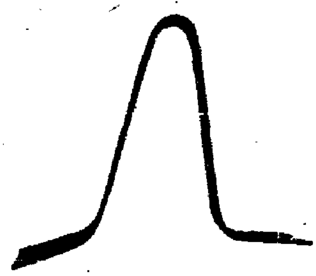


FIGURE 22
Deformed Specimen
D-43 Material
.012 Gage

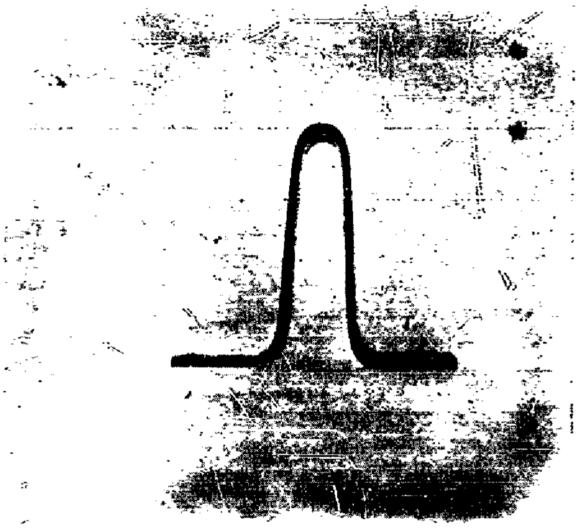


FIGURE 23
Deformed Specimen
Cb-752 Material
.018 Gage

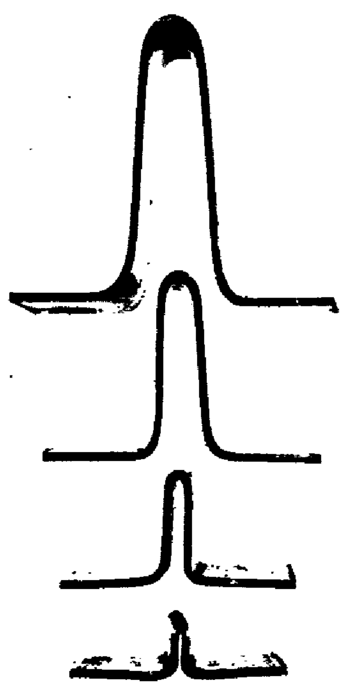


FIGURE 24
Deformed Specimens
To various bend radii
D-43 Material
.030 Gage

SECTION VIII

WORK SCHEDULE

A. NEXT PERIOD

During the next four-month period the following should be accomplished:

1. Completion of requirements study on TZM fasteners with tests through 2800°F in static and high velocity (200 feet per second) air.

2. Completion of follow-through work on requirements of columbium fasteners.

3. Fabricate, coat, and begin to test columbium threaded fasteners with electrophoretic coating.

4. Choose and process the second columbium alloy.

5. Start coating feasibility work on tantalum.

6. Test deformation specimens with coating.

7. Compare Tapco coating chemistry when applied by standard pack means by Tapco to that applied by electrophoretic process by Vitro. Tests will consist of impact on specimens and bend tests on sheet.

B. PROGRAM SCHEDULE

The entire program is scheduled for twenty four (24) months as shown in the attached schedule.

PROJECTED PROGRAM SCHEDULE FOR
STRUCTURAL FASTENING TECHNOLOGY

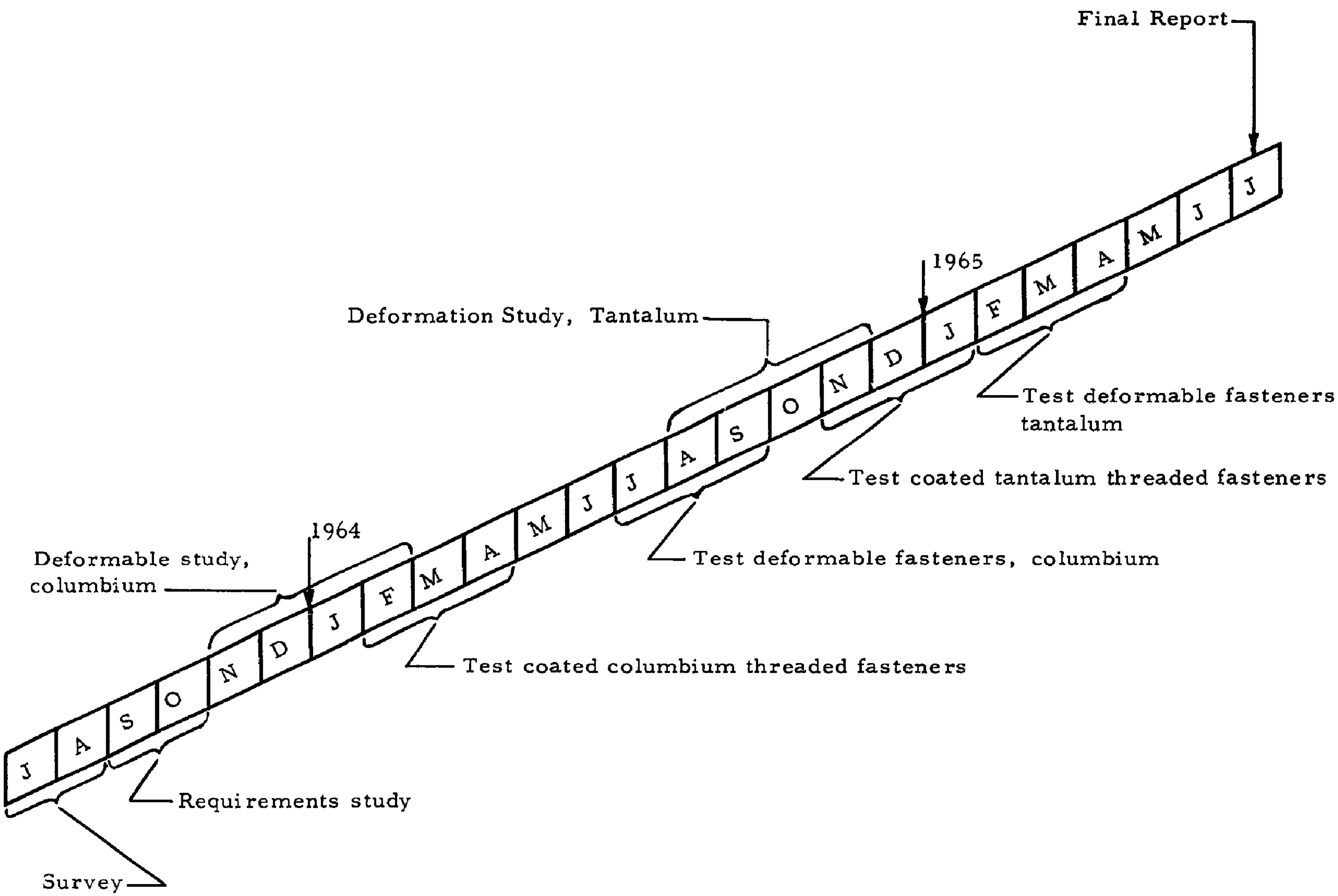


FIGURE 25

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